GAS DATA BOOK

Sixth Edition

Matheson®

LIBRARY OF CONGRESS
1800

MATHESON GAS DATA BOOK

Sixth Edition

By

William Braker
Technical Advisor, Matheson
and
Allen L. Mossman
President, Matheson

Matheson®
Division Searle Medical Products USA Inc
Lyndhurst, NJ 07071

T P761
.C65 B7
1980
Copy 2

LIBRARY OF CONGRESS
MAY 3 1 1983
COPY
COPYRIGHT OFFICE

MATHESON GAS DATA BOOK

Copyright, 1980 by Matheson. Printed in the United States of America. This book, or parts thereof, may not be reproduced in any form without the prior permission of Matheson.

Library of Congress
Catalog Card No. 80-83159

80-83159

PREFACE

Matheson takes pride and satisfaction in publishing the new sixth edition of the Matheson Gas Data Book. Thirty five years ago, Matheson offered 14 different gases. Today, Matheson offers well over 100 different gases to the world's entire scientific community whose needs have made this market the most sophisticated and dynamic market in the world. Matheson has tried to keep pace with this market's growth, and over the last thirty-five years we have been asked a lot of questions concerning gases. The Matheson Gas Data Book answers most of these questions in compiling as much information relating to gases without entering the realm of an engineering handbook.

The sixth edition of the Matheson Gas Data Book is, like previous editions, a compilation of individual gas data sheets. It is similar to previous editions in that some general information is presented in Appendices I and II relating to "General Precautions In Handling and Storage", and "Disposal Of Leaking Cylinders". We realize that this involves some repetition in the text, especially when the data cover similar gases. But we think that when you are interested in a specific gas, you want to know *all* about the gas as quickly and directly as possible. We are of the opinion that this type of presentation accomplishes this objective. Matheson offers a comprehensive data sheet on any gas available from the company, as well as some not available. Therefore, if you wish to distribute copies of any individual data sheets, simply contact Matheson and inquire about reprints.

This sixth edition differs from previous editions in that considerably more physical and thermodynamic data are reported (in SI units), as well as expanded sections on the effects in man, toxicity, and first aid suggestions.

The authors wish to thank Mrs. Augusta Braker for her kind assistance and expertise in the compilation of this 6th edition.

William Braker
Allen L. Mossman
December, 1980

CONTENTS

Preface iii
Safe Handling of Compressed Gases in Laboratory and Plant v
Symbols and Abbreviations xii
Index of Gases xix
Gas Data 1
Appendix I 710
Appendix II 711

Safe Handling of Compressed Gases in Laboratory and Plant

Before we are allowed to drive a car, most states require proof of our ability to drive. To become a proficient and safe driver, one must have skill, judgment, and driver education. We do not always consider that we are performing a hazardous operation by driving a car, yet the fact remains that many people are killed or hurt every day as a result of carelessness in handling this machine. Although the safety record of the compressed gas industry is excellent, the questions raised by the users of gas products, and the accidents that these same users are involved in, show that many of them have neither learned nor applied the safety measures which would earn them their "compressed gas handler's license".

When handled by people who are properly trained and aware of the potential hazards, compressed gases are as safe to work with as most of the ordinary chemical liquids and solids normally handled on a routine basis in any laboratory.

Cylinder safety is addressed by the supplier through his adherence to regulations set forth by the Dept. of Transportation and by his supplying cylinders with specific valves, labels and/or markings in accordance with recognized standards. It is mandatory for the supplier to ship cylinders manufactured in conformance with Department of Transportation (DOT) regulations and to follow DOT regulations in the testing and inspection of cylinders, the proper filling of these cylinders, and the use of safety devices which are approved by the Bureau of Explosives (1).

A compressed gas is defined by the Department of Transportation as "any material or mixture having in the container either an absolute pressure exceeding 40 pounds per square inch at 70 °F, or an absolute pressure exceeding 104 pounds per square inch at 130 °F, or both; or any liquid flammable material having a Reid vapor pressure exceeding 40 pounds per square inch at 100 °F "(2) (3).

For the purposes of safety, all volatile materials and mixtures packaged in cylinders should be considered compressed gases.

HAZARDS

The handling of compressed gases is more hazardous than the handling of liquid and solid material because of the following properties unique to compressed gases: pressure, diffusivity, low flash points for flammable gases, low boiling points, and no visual or odor detection of many hazardous gases.

These unique properties give rise to many hazards such as formation of explosive concentrations of flammable gases, toxicity, other physiological effects, frostbite, corrosion, irritation, and high reactivity.

CYLINDER TESTING

Hydrostatic pressure tests are performed on cylinders for most gases every five years to determine their fitness for further use. During the hydrostatic test, a cylinder is pressurized with water to a value determined by the cylinder specification and service pressure. The cylinder expands under this pressure. The expansion of the cylinder and the value of permanent expansion after the pressure is released are recorded. Tolerances on these values must be met in order to permit further use of the cylinder. These values also allow the wall thickness of the cylinder and the degree of corrosion affecting the walls to be estimated (4) (5).

CYLINDER FILLING

Nonliquefied gases may be filled to the service pressure marked on a cylinder. These markings will appear on the shoulder of the cylinder, i.e., DOT 3A-2 015, indicating the cylinder has been manufactured in accordance with DOT specification 3A, and the cylinder filling pressure is 2 015 psi at 70 °F. At present, DOT regulations on nonliquefied, nonflammable gases permit a 10% overfilling of cylinders. Liquefied gases, on the other hand, must be filled to a filling density (1). This filling density represents the maximum weight of the material permitted in the cylinder, as a percentage of the water capacity of the cylinder.

Since compressed gas cylinders are handled by a number of different types of plant personnel, it might be well to consider the precautions in handling to be taken from the time it is delivered until the time it is emptied and ready for return.

CYLINDER RECEIPT AND CONTENT IDENTIFICATION

When a cylinder is delivered to the receiving department, it should have (1) content identification by stencilling or labels, (2) a DOT label, and (3) a value protection cap. UNDER NO CIRCUMSTANCES should the means of identification be removed from the cylinder. The valve protection cap (Fig. 1) should also remain in place until the user has secured the cylinder and is ready to withdraw the contents.

Fig. 1
Cylinder Values Must Be Protected

DOT labels are required for cylinders in interstate transportation. Some states require these labels for intrastate shipments also. These labels have a minimum of precautionary handling information, and will classify the cylinder contents as flammable gas, nonflammable gas, poison gas, corrosive gas, oxidizer gas, etc. Unfortunately, there is as yet no uniformity in the identification of cylinder contents, although a standard for marking compressed gases is available (6). Some suppliers provide adequate stencilling or labels with as much information on them as possible, warning against possible hazards associated with the cylinder contents. On the other hand, cylinders may be received with no identification other than a color code. Under no circumstances should such cylinders be accepted. Color codes are of value only in helping the supplier to segregate large numbers of cylinders into various gas services.

CYLINDER STORAGE(7)(8)(9)(10)

After cylinders are received, they are usually placed in storage either in a special gas storage area or in the laboratory itself. Some plants have elaborate gas storage areas provided in a separate building or in part of the laboratory. Storage buildings or areas should be (a) fire resistant, (b) well-ventilated, (c) located away from sources of ignition or excessive heat, and (d) dry. Indoor storage areas should not be located near boilers, steam or hot water pipes or any sources of ignition. Outdoor storage areas should have proper drainage, and should be protected from the direct rays of sun, in localities where high temperatures prevail (Fig. 2).

Fig. 2

Areas that are not under surveillance twenty-four hours a day should not have any open flames or sparking equipment in any locations to which leaking gas could diffuse and become ignited or explode. Subsurface storage locations should be avoided. Cylinders should be protected against tampering by unauthorized personnel. Cylinders should be chained in place or put in partitioned cells to prevent them from falling over (Fig. 3) (9).

Storage in a laboratory should be confined to only those cylinders in use. In all cases, storage areas should comply with applicable federal, state, local, and municipal requirements.

Fig. 3
Stabilize Cylinders
Model 6512 Cylinder Station

GENERAL PRECAUTIONS FOR HANDLING & STORAGE

1. Never drop cylinders or permit them to strike each other violently. (Fig. 4)

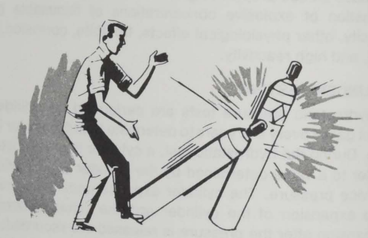


Fig. 4
Don't Drop

2. Cylinders may be stored in the open but, in such cases, should be protected against extremes of weather and, to prevent rusting, from the dampness of the ground. Cylinders should be stored in the shade in areas where extreme temperatures are prevalent.
3. The valve protection cap should be left on each cylinder until it has been secured against a wall or bench, or placed in a cylinder stand, and is ready to be used.

Matheson

4. Avoid dragging, rolling, or sliding cylinders, even for a short distance. They should be moved by using a suitable hand truck (Fig. 5).

Fig. 5
Transport Correctly

5. Never tamper with safety devices in valves or cylinders (Fig. 6).
6. Do not store full and empty cylinders together. Serious suckback can occur when an empty cylinder is attached to a pressurized system.
7. No part of a cylinder should be subjected to a temperature higher than 125°F. A flame should never be permitted to come in contact with any part of a compressed gas cylinder.

Fig. 6
Never Tamper with Safety Devices in Cylinders or Valves

8. Do not place cylinders where they may become part of an electric circuit. When electric arc welding, precautions must be taken to prevent striking an arc against a cylinder.

INTRAPLANT TRANSPORTATION

When moving cylinders from a storage area into the plant or laboratory, make sure the valve protection cap is in place. The cylinder should then be transported by means of a suitable hand truck such as that shown in Figure 5. Such a hand truck should be provided with a chain or belt for securing the cylinder so that it cannot fall if the hand truck happens to pass over a bump. If a large number of cylinders must be moved from one area to another, a power device such as shown in Figure 7 can be used.

A number of different devices have been developed for transporting groups of cylinders. All incorporate some means of securing cylinders to prevent them from falling over (for example, an adjustable chain or special saddle, designed to cradle cylinder) (9). When the cylinder is brought to its place

Fig. 7

of use in the laboratory or plant, it should be secured to a wall, a bench, or some other firm support. A plain chain or a bench clamp and belt (Matheson Model 508 cylinder holder) should be used. In all cases make sure that the chain or belt is located high enough on the cylinder body so that the cylinder cannot possibly tumble out of it (Fig. 8). Figure 8 shows the special Matheson Model 6501 stand. This stand is adaptable to a number of different size cylinders by means of an adjustable

Fig. 8
Model 6501 Cylinder Stand

support strap. Although a stand is not as effective as securing a cylinder to a wall or bench, it does improve cylinder stability in situations where other types of support are impractical. Once the cylinder is secured, the cap may be removed, exposing the valve.

CYLINDER VALVES

Figure 9 shows four basis types of cylinder valves. They each differ in outlet type and safety device. The Compressed Gas Association (CGA) has standardized various outlets for different families of gases to prevent interchange of regulator equipment between gases which are not compatible. These standards have also been adopted by the American National Standards Association (ANSI) (11). The use of adapters defeats the intent of varying outlet designs, and adapters should be

Matheson

Fig. 9

used *with care* only on gases definitely known to be compatible. Equipment for certain gases, such as Oxygen, should never be interchanged for use on other compressed gases. Gases which are oil-pumped can cause an oil film to coat the internal parts of regulators and associated equipment and, if this equipment is then used with Oxygen, a fire or explosion is liable to occur.

CYLINDER SAFETY DEVICES

Safety devices are incorporated into all DOT approved compressed gas containers, except those in poison or toxic gas service, where the danger of exposure to fumes is considered more hazardous than that of a potential cylinder failure. Gases for which safety devices are not permitted usually require cylinders having a higher safety factor than do cylinders for other compressed gases.

Safety devices are incorporated in the cylinder valve, in plugs in the cylinder itself, or both. In certain types of gas service, and in cylinders over a particular length, two safety devices may be required, one at each end of the cylinder.

The safety devices used in DOT approved cylinders are approved by the Bureau of Explosives (12). These safety devices are of four basis types as follows: (1) Safety relief, used mostly for low pressure, liquefied, flammable gases, (2) frangible disc, used mostly for high pressure cylinders, (3) frangible disc backed up by a fusible metal, used in high pressure cylinders, and (4) fusible metal. The safety relief type consists of a spring-loaded seat which opens to relieve excessively high pressure and then closes when the pressure returns to a safe value. The frangible disc will burst considerably above the service pressure but below or at the hydrostatic test pressure of a cylinder, and will release the entire cylinder contents. The frangible disc backed up by fusible metal will function only if the temperature is hot enough to melt the fusible metal, after which excessive pressures will burst the disc, causing the entire cylinder contents to be released. The fusible metal device melts away at excessive temperatures, allowing the entire cylinder contents to escape. Any of these safety devices will prevent a cylinder from bursting due to excessively high temperatures. However, numbers 3 and 4 may not prevent a cylinder from bursting in cases where an overfilled cylinder is exposed to a temperature which is excessive but not high enough to melt the safety devices. Since the proper function of cylinder safety devices depends to a large extent on the proper filling of the cylinder, *such filling should never be attempted by the user unless express permission has been obtained from the gas supplier.* Safety devices may also fail to function properly if an intense flame impinging on the side wall of a cylinder weakens the metal to the point of failure before heat or pressure can cause the safety device to function properly.

KNOW THE GAS YOU WILL BE HANDLING

It is of the utmost importance that those properties of a compressed gas that represent hazards (such as flammability, toxicity, chemical activity, and corrosive effects) be well known to the gas user. Every attempt should be made to learn these various properties before the gas is used. It is sometimes difficult to determine the major hazard of any one gas, since this factor is influenced a great deal by how the gas is used. In a laboratory hood in the presence of an open flame, the flammability of Carbon Monoxide might well be the major hazard, whereas in a pilot plant run using Carbon Monoxide as a reactant, leakage, and therefore toxicity, may represent the major hazard.

It is interesting to note in Figure 10 the flammability ranges of various gases (13). Although the flammability ranges of the liquefied petroleum gases such as Butane and Propane are relatively short, only very small concentrations are necessary to create flammable mixtures. The flammability ranges of Acetylene, Carbon Monoxide, Ethylene Oxide, Hydrogen Sulfide, and Hydrogen are extremely long, indicating that they can form explosive mixtures with Air under a wide variety of conditions.

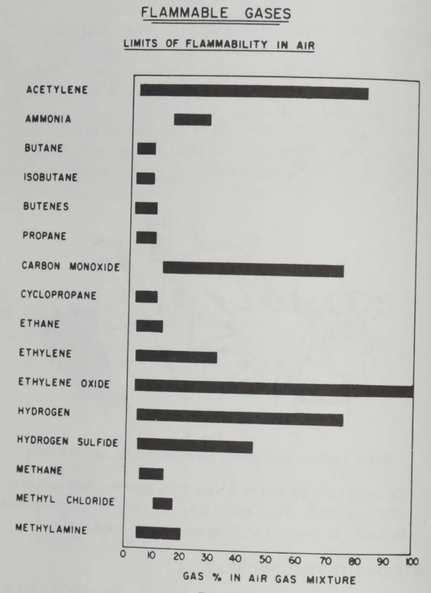


Fig. 10

Along with the properties of different gases, it is important to know what materials of construction must be used with many of them to prevent equipment failure due to corrosion. Another important factor in the choice of materials of construction concerns the possible formation of hazardous compounds, such as Acetylides formed by the reaction of copper with Acetylene or gases containing Acetylene as an impurity (14), or the possible formation of fulminates when Mercury is used in the presence of Ammonia.

The hazards of toxic, flammable, and corrosive gases can be minimized by working in well-ventilated areas. Where possible, work should be done in a hood, employing cylinder sizes that will assure use of all the gas within a reasonable amount of time (Fig. 11).

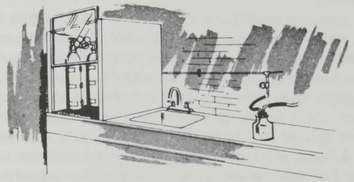


Fig. 11

Leaks should not be allowed to go unchecked. The use of a suitable leak detector is advised (Fig. 12). Advise the supplier immediately of cylinder leaks that cannot be stopped by simple adjustments, such as tightening a packing nut.

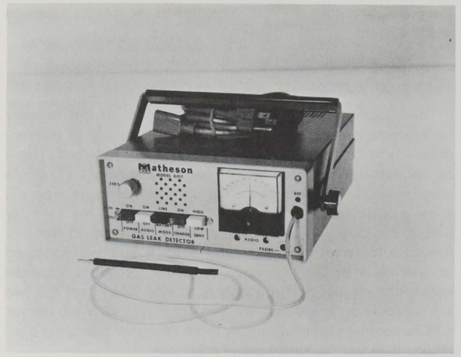


Fig. 12
Model 8017 Leak Detector

When using toxic gases, it is advisable that a toxic gas detector or indicator be used to give warning of the presence of toxic gas concentrations. For example, strips of lead acetate paper can be hung in an area where Hydrogen Sulfide is being used. Although this gas has a disagreeable odor, it soon deadens the sense of smell, rendering the user incapable of detecting increasingly dangerous concentrations by odor.

When corrosive gases are being used, the cylinder valve stem should be worked frequently to prevent freezing. The cylinder valve should be closed when the cylinder is not in use. Regulators and valves should be flushed with Dry Air or Nitrogen after use in corrosive service. Such control devices should not be left on a cylinder, except when the cylinder is in frequent use. When corrosive gases are to be discharged into a liquid, a trap, check valve, or vacuum break device should always be employed to prevent dangerous suckback (Fig. 13).

Fig. 13

"PREVENTATIVE PREPAREDNESS" IN THE PLANT OR LABORATORY

The user of compressed gases should familiarize himself with the first aid methods to be employed in cases of overexposure or burns caused by a gas. A plant or company doctor should be familiar with whatever further treatments may be necessary. Unnecessary delay in the treatment of a patient overcome by a toxic gas or burned by a corrosive gas could cause the patient permanent damage, and might even result in death. Authorized personnel should administer first aid; however, they should not take it upon themselves to administer medical treatments. A physician should be contacted immediately.

Gas masks should be kept on hand in a location which is accessible in case an area becomes contaminated. The proper type of gas mask should be used and those involved in the handling of compressed gases should familiarize themselves with the proper application and limitations of the various types of masks and respiration equipment available.

To prevent eye damage due to equipment failure, safety glasses should always be worn when working with compressed gases.

Eye-baths and safety showers should be located nearby, but out of the immediate area which is likely to become contaminated in the event of a large release of gas.

Fire extinguishers, preferably of the dry chemical type, should be kept close by, and should be checked periodically to insure their proper operation.

PROPER DISCHARGE OF CYLINDER CONTENTS

LIQUEFIED GASES

For controlled removal of the liquid phase of a liquefied gas, a manual valve is used (Fig. 14). Special liquid flow regulators are also available. It must be remembered that withdrawal of liquid must necessarily be done at the vapor pressure of the material. Any attempt to reduce the pressure will result in flashing of all or part of the liquid to the gas phase.

Rapid removal of the gas phase from a liquefied gas may cause the liquid to cool too rapidly causing the pressure and flow to drop below the required level. In such cases, cylinders may be heated in a water bath with temperature controlled to no higher than 125 °F. Rapid gas removal can also be effected by transferring the liquid to a heat exchanger, where the liquid is vaporized to a gas. This method imposes no temperature limitations on the material; however, care should be taken to prevent blockage of the gas line downstream of the heat exchanger as this may cause excessive pressure to build up in both the heat exchanger and the cylinder. Safety relief devices

Fig. 14
Manual Needle Valve

should be installed in all liquid transfer lines to relieve sudden, dangerous hydrostatic or vapor pressure build ups.

NONLIQUEFIED GASES

The most common device used to reduce pressure to a safe value for gas removal is an automatic pressure regulator. This device is shown in Figure 15. It consists of a spring (or gas) loaded diaphragm which controls the throttling of an orifice. Delivery pressure will exactly balance the delivery pressure spring to give a relatively constant delivery pressure.

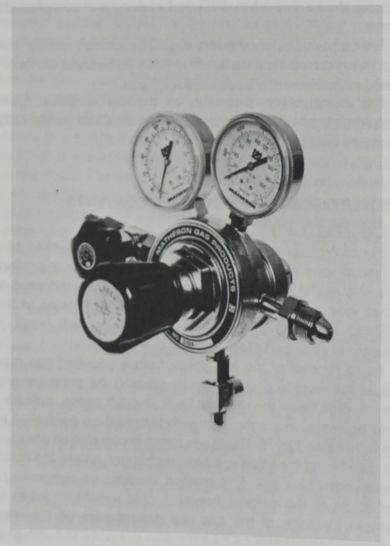


Fig. 15
Automatic Pressure Regulator
Model 3104

AUTOMATIC REGULATOR HANDLING AND USE

A regulator should be attached to a cylinder without forcing the threads. If the inlet of a regulator does not fit the cylinder, no effort should be made to try to force the fitting. A poor fit may indicate that the regulator is not intended for use on the gas chosen.

The following procedure should be used to obtain the required delivery pressure: (1) After the regulator has been attached to the cylinder valve outlet, turn the delivery pressure adjusting screw counterclockwise until it turns freely. (2) Open the cylinder valve slowly until the tank gauge on the regulator registers the cylinder pressure. At this point, the cylinder pressure should be checked to see if it is at the expected value. A large error may indicate that the cylinder valve is leaking. (3) With the flow control valve at the regulator outlet closed, turn the delivery pressure adjusting screw clockwise until the required delivery pressure is reached. Control of flow can be regulated by means of a valve supplied in the regulator outlet or by a supplementary valve put in a pipeline downstream from the regulator. The regulator itself should not be used as a flow control by adjusting the pressure to obtain different flow rates. This defeats the purpose of the pressure regulator, and in some cases where higher flows are obtained in this manner, the pressure setting may be in excess of the design pressure of the system.

TYPES OF AUTOMATIC REGULATORS

The proper choice of regulator depends on the delivery pressure range required, the degree of accuracy of delivery pressure to be maintained, and the flow rate required. There are two basic types of automatic pressure regulators: (1) single stage and (2) double or two stage. The single stage type will show a slight variation in delivery pressure as the cylinder pressure drops. It will also show a greater drop in delivery pressure than a two stage regulator as the flow rate is increased as well as a higher "lock-up" pressure (pressure increase above delivery set point necessary to stop flow) than the two stage regulator. In general, the two stage regulator will deliver a more constant pressure under more stringent operating conditions than will the single stage regulator.

MANUAL FLOW CONTROLS

Where intermittent flow control is needed and an operator will be present at all times, a manual type of flow control may be used. This type of control (illustrated in Figure 14) is simply a valve which is operated manually to deliver the proper amount of gas. Fine flow control can be obtained but it must be remembered that dangerous pressures can build up in a closed system or in one that becomes plugged, since no means are provided for automatic prevention of excessive pressures.

MATERIALS OF CONSTRUCTION

Aside from the type of control required, the proper material of construction must be considered. For example, intergranular attack of brass will occur in Ammonia or Methylamine service. In such cases, steel or aluminum are used as materials of construction for regulators or valves. The proper materials of construction must be carried through for all pipe lines, valves, and other accessories being used in the gas system.

Matheson

SAFETY DEVICES

It is necessary to provide further supplementary safety devices to prevent overpressurizing of lines, and to prevent suckback of materials into cylinder controls, and possibly the cylinder itself. Aside from the possibility of causing rapid corrosion, the reaction of a gas with material that has been sucked back may be violent enough to cause extensive equipment and cylinder damage. The danger of suckback can be eliminated by providing a trap (12) which will hold all material that can possibly be sucked back, or by using a check valve or suitable vacuum break. Pressure increases due to uncontrolled reactions or unexpected surges of pressure can be relieved by means of a safety relief device installed in the gas line. For experiments conducted in glassware, such a pressure relief device can be improvised by using a U-tube filled with mercury or other inert liquid, with one end attached by means of a "T" to the gas line, and with the other end free to exhaust into an open flask which will contain the mercury in case of overpressure. For systems, under higher pressure, devices such as spring-loaded relief valves or frangible discs are recommended.

DETERMINATION OF CYLINDER CONTENT

NONLIQUEFIED GASES

As the content of a cylinder of nonliquefied gas is discharged, the cylinder pressure decreases by an amount proportional to the amount withdrawn. The cylinder should be considered empty while positive pressure (25 psig or greater) still remains in order to prevent suckback and contamination. Failure to close the valve on an empty cylinder will allow air and moisture to be drawn into the cylinder as it "breathes" during temperature changes; an explosive mixture may build up if the gas is flammable; and an extremely corrosive condition will be created in cylinders which contain Chlorine, Hydrogen Chloride, or other acid forming or corrosive gases.

LIQUEFIED GASES

As the vapor phase of a liquefied gas is withdrawn from a cylinder, the cylinder pressure or vapor pressure will remain constant as long as any liquid is present. This condition holds true if the temperature does not vary. If, however, the material is withdrawn from the cylinder at a rapid rate, the material itself will supply the heat for vaporization and upon subsequent cooling, the vapor pressure will be lowered. It is, therefore, impossible to determine the content of a cylinder containing a liquefied gas, except by weighing. For this purpose, the Matheson Cylinder Scale Model 8510 is recommended (Fig. 16). Cylinders containing liquefied gases are stamped or tagged with the tare weight in order to allow the content to be determined.

An indication of cylinder content depletion for some high pressure liquefied gases such as Carbon Dioxide, Ethane, and Nitrous Oxide can be obtained by noting the cylinder pressure. After depletion of the liquid phase, the cylinder pressure will decrease below the normal vapor pressure, as long as the contents have not been withdrawn rapidly before the cylinder pressure is noted. A cylinder containing Carbon Dioxide will have approximately 20% of its original content remaining after depletion of the liquid phase.

As with cylinders of nonliquefied gases, cylinders containing liquefied gases should never be completely emptied, in order to prevent suck-back and contamination of the cylinder.

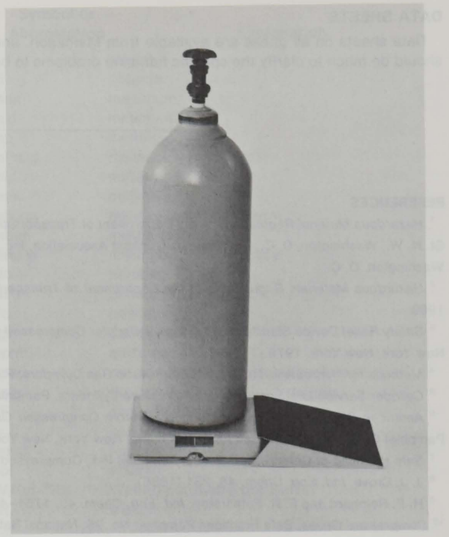


Fig. 16
Model 8510 Cylinder Scale

HANDLING OF EMPTY CYLINDERS

Where cylinders are considered empty, the valves should be closed. Valve protection caps, outlet dust caps, and other accessories shipped with the cylinder should be attached to the cylinder as received. The cylinder should be marked or labeled "EMPTY". Cylinders should then be placed in a proper storage area, segregated from full cylinders, to await pick-up for return to the supplier (Fig. 17).

Fig. 17
Return in Condition Received

Carelessness in the handling of an empty cylinder could result in its being mistaken for a full cylinder. The connecting of an empty cylinder to a high pressure system could cause foreign materials to back up into the cylinder, resulting in all the attendant hazards of suckback, and possible violent reaction within the cylinder.

NEVER TAKE CHANCES

In any emergency, or conditions creating problems not readily solved, always contact the gas supplier for instructions, or information; do not attempt to handle the situation without further aid.

Matheson

DATA SHEETS

Data sheets on all gases are available from Matheson, and should do much to clarify the specific handling problems to be encountered for specific gases. They should be consulted before attempting to handle gases with which the user is unfamiliar.

REFERENCES

[1] *Hazardous Material Regulations of the Department of Transportation,* R. M. Graziano Tariff No. 27 issued by R. M. Graziano, Agent, 1920 "L" St. N. W., Washington, D. C., or American Trucking Association, Inc., Tariff A.T.A. 111-A, issued by R. H. Hinchcliff, Agent, 1616 "P" St. N. W., Washington, D. C.

[2] *Hazardous Materials Regulations of the Department of Transportation,* Agent T. C. George's Tariff No. 23, issued by T. C. George, Agent, 1969.

[3] *Safety Relief Device Standards,* Part 1, *Cylinders for Compressed Gases,* 6th Edition, Pamphlet S-1, Part 1, Compressed Gas Association, Inc., New York, New York, 1979.

[4] *Methods for Hydrostatic Testing of Compressed Gas Cylinders,* Pamphlet C-1, Compressed Gas Association, Inc., New York, New York, 1975.

[5] *Cylinder Service Life-Seamless, High-pressure Cylinders,* Pamphlet C-5, Compressed Gas Association, Inc., New York, New York, 1976.

[6] *American Standard Method of Marking Portable Compressed Gas Containers to Identify the Material Contained,* ASA, Z48.1-154, C.G.A. Pamphlet C-4, Compressed Gas Association, Inc. New York, New York, 1978.

[7] *Safe Handling of Compressed Gases,* Pamphlet P-1, Compressed Gas Association, Inc., New York, New York, 1974.

[8] J. J. Crove, *Ind. Eng. Chem. 48,* 231 (1956).

[9] H. F. Reinhard and F. R. Fetherston, *Ind. Eng. Chem. 49,* 1751–4 (1957).

[10] *Compressed Gases,* Safe Practices Pamphlet No. 95, National Safety Council, Chicago, Illinois.

[11] *American Standard Compressed Gas Cylinder Valve Outlet and Inlet Connection,* ASA B57.1-1957, C. G. A. Pamphlet V-1, Compressed Gas Association, Inc., New York, New York, 1978 Appended.

[12] *Safety Relief Device Standards,* Part 1-*Cylinders for Compressed Gases,* Pamphlet S-1, Part 1, Compressed Gas Association, Inc., New York, New York.

[13] H. F. Coward and G. W. Jones, *Limits of Flammability of Gases and Vapors,* Bulletin 503, Bureau of Mines, Government Printing Office, Washington, D. C.

[14] V. F. Brameld, *et al., Soc. Chem. Ind.* (London) *66,* 346–353 (1946).

RELATED REFERENCES

Other references (for those wishing to pursue further the safe handling of gases, their properties, and detection) are listed below.

1. M. B. Jacobs, *The Analytical Chemistry of Industrial Poisons, Hazards and Solvents, 1949,* John Wiley & Sons, Inc., New York, New York.
2. Y. Henderson and H. W. Haggard, *Noxious Gases and the Principles of Respiration Influencing Their Action,* 2nd edition, *1943,* Reinhold Publishing Corporation, New York, New York.
3. F. A. Patty, editor, *Industrial Hygiene and Toxicology, 1962,* Volume 2, John Wiley & Sons, Inc., New York, New York.
4. *Standards for the Storage and Handling of Liquefied Petroleum Gases,* Bulletin No. 58, *May 1954,* National Fire Protection Association, Boston, Massachusetts.
5. N. I. Sax, *Dangerous Properties of Industrial Materials,* 4th edition, *1975,* Van Nostrand Reinhold, New York, New York.
6. M. B. Jacobs, *The Analytical Toxicology of Industrial Inorganic Poisons, 1967,* John Wiley & Sons, Inc. New York, New York.
7. W. Braker and A. L. Mossman, *Matheson Gas Data Book,* 5th edition, *1971,* Matheson, East Rutherford, New Jersey.
8. W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment,* 2nd edition, *1977,* Matheson, Lyndhurst, New Jersey.

SYMBOLS AND ABBREVIATIONS

The following symbols and abbreviations are used in this Gas Data Book:

Symbol or Abbreviation	Explanation
Å	angstroms
abs	absolute
ACGIH	American Conference of Governmental Industrial Hygienists
ASME	American Society of Mechanical Engineers
atm	atmosphere(s)
bar	bar(s)
bar (g)	bar(s) gauge pressure
BP	Boiling Point
Btu	British thermal unit(s)
°C	degree Celcius
cal	calorie(s)
cP	centipoise
cm^3	cubic centimetre(s)
CGA	Compressed Gas Association
cm	centimetre(s)
C_p	specific heat at constant pressure
C_v	specific heat at constant volume
DOT	Department of Transportation
dyn/cm	dyne(s) per centimetre
D	Debye(s)
°F	temperature, degrees Fahrenheit
ft	foot, feet
IPS	iron pipe size
°K	Kelvin
kcal	kilocalorie(s)
kJ/mol	kilojoule(s) per mole
kg/m^3	kilogram(s) per cubic metre
J/(mol·°K)	joule(s) per mole per Kelvin
kg	kilogram(s)
kJ/kg	kilojoule(s) per kilogram
kPa	kilopascals
l	litre(s)
lb	pounds
max	maximum
min	minimum
mp	melting point
mPa·s	millipascal-second(s)
ml	millilitre(s)
mm	millimetre(s)
mN/m	millinewton(s) per metre
mbar	millibar(s)
mmHg	millimetre(s) of mercury
No.	number
NPT	national pipe thread
Pa	pascals
(g)	gauge pressure
ppm	parts per million
psia	pounds per square inch absolute
psig	pounds per square inch gauge
°R	degrees Rankine
s	second(s)
temp.	temperature
vol	volume
W/(m·°K)	Watt(s) per metre per Kelvin
wt.	weight

Presentation Of The Physical And Thermodynamic Properties Of The Gases

In some industries, both here and abroad, the U. S. customary units are gradually being replaced by those of a modernized metric system known as the International System of Units (SI). Since SI is rapidly being adopted for the teaching of science and engineering in schools, colleges, and universities throughout the world, the physical and thermodynamic data have been presented in terms of the more coherent SI units. However, other customary units have generally also been listed, or methods for conversion of SI units to other units are indicated.

A description and definition of SI base units and supplementary units appears directly after the preface, followed by a tabulation of various SI derived units, SI prefixes, non-SI units, definition of SI derived units, and an alphabetical list of units and their conversion factors. In the latter list, relationships that are exact are followed by an asterisk; relationships that are not followed by an asterisk are either the results of physical measurements or are only approximate.

It will be observed throughout the presentation of the data that to facilitate the reading of numbers having four or more digits, the digits have been placed in groups of three separated by a space instead of commas counting both to the left and to the right of the decimal point.

It should also be noted that the bar as used throughout this text is the *absolute* bar, except in those instances where bar is followed by the symbol (g) in which case it denotes bar gauge pressure.

The data for the conversion factors have been obtained primarily from three sources, namely,

(1) *ASTM Standard Metric Practice Guide E-380, 1974,*

(2) M. L. McGlashan in *Kirk-Othmer's Encyclopedia of Chemical Technology*, second revised edition, *1971*, Supplement Volume, pp. 984–1007, John Wiley & Sons, Inc., New York, N. Y.,

(3) *The International Systems of Units*, National Bureau of Standards Special Publication 330, *1972*, C. H. Page and P. Vigoureux, editors.

It is hoped that this presentation in terms of SI units will help to stimulate their more rapid adoption for use by science and industry in the United States.

William Braker
Allen L. Mossman
1980

Units and Conversion Factors

The SI base units are as follows:

Base Unit

Physical Quantity	Name of SI Base Unit	Symbol for SI Base Unit
length	metre	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
thermodynamic temperature	kelvin	°K
luminous intensity	candela	cd
amount of substance	mole	mol
Supplementary Units		
plane angle	radian	rad
solid angle	steradian	sr

Definitions Of The SI Base And Supplementary Units

Metre—The metre is the length equal to 1 650 763.73 wavelengths in vacuum of the radiation corresponding to the transition between the levels $2p_{10}$ and $5d_5$ to the Krypton-86 atom.

Kilogram—The kilogram is the unit of mass; it is equal to the mass of the international prototype of the kilogram. The international prototype of the kilogram is a certain piece of platinum-iridium kept at the International Bureau of Weights and Measures at Serves, near Paris.

Second—The second is the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the Cesium-133 atom.

Ampere—The ampere is that constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed one metre apart in a vacuum, would produce between these conductors a force equal to 2×10^{-7} newtons per metre of length.

Kelvin—The unit of thermodynamic temperature is the kelvin. It is the fraction 1/273.16 of the triple-point of water.

Candela—The candela is the luminous intensity, in the perpendicular direction, of a surface 1/6000 000 square metres of a black body at the temperature of freezing platinum under a pressure of 101 325 newtons per square metre.

Radian—The radian is the unit of measure of a plane angle with its vertex at the center of a circle and subtended by the arc equal in length to the radius.

Steradian—The steradian is the unit of measure of a solid angle with its vertex at the center of a sphere and enclosing an area of the spherical surface equal to that of a square with sides equal in length to the radius.

Mole—The mole is the amount of substance of a system which contains as many elementary entities as there are carbon atoms in 0.012 kilogram of Carbon-12. The elementary entity must be specified, e.g., one mole of Hg^+ has a mass equal to 0.200 59 kilogram; one mole of HgCl has a mass equal to 0.236 04 kilogram; one mole of Hg_2Cl_2 has a mass equal to 0.472 08 kilogram.

Matheson

SI DERIVED UNITS

The SI Derived Units are those derived by appropriate multiplication and division of the SI Base Units, and shown below.

Quantity	Unit	Symbol	Formula
activity	disintegration per second	—	(disintegration/s)
density	kilogram per cubic metre	—	kg/m^3
electric potential difference	volt	V	W/A
electric resistance	ohm	Ω	V/A
electromotive force	volt	V	W/A
energy	joule	J	N·m
entropy	joule per newton	—	J/N
force	newton	N	$kg \cdot m/s^2$
frequency	hertz	Hz	(cycle)/s
pressure	pascal	—	Pa
quantity of electricity	coulomb	C	A·s
quantity of heat	joule	J	N·m
specific heat	joule per kilogram kelvin	—	J/(kg·°K)
thermal conductivity	watt per metre kelvin	—	W/(m·°k)
velocity	metre per second	—	m/s
viscosity, dynamic	pascal-second	—	Pa·s
viscosity, kinematic	square metre per second	—	m^2/s
voltage	volt	V	W/A
volume	cubic metre	—	m^3
wavenumber	reciprocal metre	—	(wave)/m
work	joule	J	N·m

The SI prefixes shown below have been approved by the CGPM to indicate multiples or submultiples of SI Base Units or of the SI Derived Units.

Multiple and Submultiple Units

Multiplication Factors	Prefix	SI Symbol
$1\,000\,000\,000\,000 = 10^{12}$	tera	T
$1\,000\,000\,000 = 10^{9}$	giga	G
$1\,000\,000 = 10^{6}$	mega	M
$1\,000 = 10^{3}$	kilo	k
$100 = 10^{2}$	hecto	h
$10 = 10^{1}$	deka	da
$0.1 = 10^{-1}$	deci	d
$0.01 = 10^{-2}$	centi	c
$0.001 = 10^{-3}$	milli	m
$0.000\,001 = 10^{-6}$	micro	μ
$0.000\,000\,001 = 10^{-9}$	nano	n
$0.000\,000\,000\,001 = 10^{-12}$	pico	p
$0.000\,000\,000\,000\,001 = 10^{-15}$	femto	f
$0.000\,000\,000\,000\,000\,001 = 10^{-18}$	atto	a

NON-SI UNITS

These units, shown below, are not coherent with SI units and their use should be discouraged.

Physical Quantity	Name of Unit	Symbol	Definition of Unit in Terms of SI Units
angle	degree	°	$(\pi/180)$rad
	minute	′	$(\pi/10\,800)$rad
	second	″	$(\pi/648\,000)$rad
length	yard	yd	0.914 4 m
	foot	ft	0.304 8 m
	inch	in	0.025 4 m
	mile	mile	1 609.344 m
	nautical mile	n mile	1 852 m
mass	pound	lb	0.453 592 37 kg
time	minute	min	60 s
	hour	h	3 600 s
	day	d	86 400 s
force	kilogram-force	kgf	9.806 65 N
	kilopond	kp	9.806 65 N
	pound-force	lbf	≈4.448 22 N
pressure	atmosphere	atm	101 325 N/m^2
	torr	Torr	≈133.322 N/m^2
	techn.atmosphere	at	98 066.5 N/m^2
	pound-force per square inch (psi)	lbf/in^2	≈6 894.76 N/m^2
	millimeter of mercury	mmHg	≈133.322 N/m^2
	inch of water	inH_2O	≈249.089 N/m^2

Definitions of SI Derived Units

Electrical potential difference (electromotive force)—The volt (unit of electric potential difference and electromotive force) is the difference of electric potential between two points of a conductor carrying a constant current of one ampere, when the power dissipated between these points is equal to one watt.

Electric resistance—The ohm is the electric resistance between two points of a conductor when a constant difference of potential of one volt, applied between these two points, produces in this conductor a current of one ampere, this conductor not being the source of any electromotive force.

Energy—The joule is the work done when the point of application of a force of one newton is displaced a distance of one metre in the direction of the force.

Force—The newton is that force which, when applied to a body having a mass of one kilogram, gives it an acceleration of one metre per second per second.

Frequency—The hertz is a frequency of one cycle per second.

Power—The watt is the power which gives to the production of energy at the rate of one joule per second.

Quantity of electricity—The coulomb is the quantity of electricity transported in one second by a current of one ampere.

Matheson

The International Committee of Weights and Measures has recommended the pascal (Pa) as the name for the unit of pressure or stress instead of the newton per square metre or bar, and the name siemens (S) as the name for the unit of electrical conductance instead of the reciprocal ohm or the ampere volt.

Pressure—The pascal is the pressure or stress of one newton per square metre.

Alphabetical List Of Units

(Symbols of SI units given in parentheses)

To convert from	to	Multiply by
ampere (Int. of 1948)	ampere (A)	0.999 835
angstrom Å	metre (m)	1×10^{-10} *
atmosphere (normal)	pascal (Pa)	101 325 *
bar	pascal (Pa)	100 000 *
bar	kilopascal (kPa)	100 000 *
British thermal unit (Int. Table)	joule (J)	1 055.056
British thermal unit (mean)	joule (J)	1 055.87
British thermal unit (thermochemical)	joule (J)	1 054.350
British thermal unit (39 °F)	joule (J)	1 059.67
British thermal unit (60 °F)	joule (J)	1 054.68
calorie (Int. Table)	joule (J)	4.186 800 *
calorie (mean)	joule (J)	4.190 02
calorie (thermochemical)	joule (J)	4.184 000 *
calorie (15 °C)	joule (J)	4.185 80
calorie (20 °C)	joule (J)	4.181 90
calorie, kilogram (Int. Table)	joule (J)	4 186.800 *
calorie, kilogram (mean)	joule (J)	4 190.02
calorie, kilogram (thermochemical)	joule (J)	4 184.000 *
centimetre of mercury (0 °C)	pascal (Pa)	1 333.22
centimetre of water (4 °C)	pascal (Pa)	98.063 8
centipoise (cP)	newton-second/metre^2 (N·s/m^2)	1.000×10^{-3} *
centipoise (cP)	millipascal-second (mPa·s)	1.000
curie	disintegration/second	3.700×10^{-10} *
day (mean solar)	second (s)	86 400
debye D	coulomb-metre (C·m)	$3.335\,64 \times 10^{-30}$
decibar	pascal (Pa)	1.000×10^{4} *
decimetre^3	metre^3 (m^3)	1.000×10^{-3} *
degree (angle)	radian (rad)	0.017 453 29
degree Celcius (°C)	kelvin (°K)	°K = °C + 273.15
degree Fahrenheit (°F)	degree Celcius	°C = ⅝ (°F − 32)
degree Fahrenheit (°F)	kelvin (°K)	°K = ⅝ (°F + 459.67)
degree Rankine (°R)	kelvin (°K)	°K = ⅝ °R
dyne	newton (N)	1×10^{-5} *
electron volt ev	joule (J)	$1.602\ 10 \times 10^{-19}$
foot (ft)	metre (m)	0.304 800 *
foot of water (39.2 °F)	pascal (Pa)	2 988.98
grain	kilogram (kg)	$6.479\ 891 \times 10^{-5}$ *
gram	kilogram (kg)	1.000×10^{-3} *
hour (mean solar)	second (s)	3 600.000
inch	metre (m)	2.540×10^{-2} *
inch of mercury (32 °F)	pascal (Pa)	3 386.389
inch of mercury (60 °F)	pascal (Pa)	3 376.85
inch of water (39.2 °F)	pascal (Pa)	249.082
inch of water (60 °F)	pascal (Pa)	248.84
joule (Int. of 1948)	joule (J)	1.000 165
kelvin (°K)	degree Celcius (°C)	°C = °K − 273.15
kelvin (°K)	degree Fahrenheit (°F)	°F = ⅝ (°K − 273.15) + 32
kilocalorie (Int. Table)	joule (J)	4 186.800 *
kilocalorie (mean)	joule (J)	4 190.02
kilocalorie (thermochemical)	joule (J)	4 184.000 *
kilogram-force (kgf)	newton (N)	9.806 650 *
kilogram-mass	kilogram (kg)	1.000 *
kilopond-force	newton (N)	9.806.650 *
liter (dm^3)	metre^3 (m^3)	1.000×10^{-3} *
micron (μ)	metre (m)	1.000×10^{-6} *
millibar	pascal (Pa)	100.000 *
millibar	kilopascal (kPa)	0.100 *
millimetre of mercury (0 °C)	pascal (Pa)	133.322 4
minute (angle)	radian (rad)	$2.908\ 882 \times 10^{-4}$
minute (mean solar)	second (s)	60.000
ohm (int. of 1948)	ohm (Ω)	1.000 495
pascal (Pa)	newton/metre^2 (N/m^2)	1.000 *
poise (abs. viscosity)	pascal-second (Pa·s)	0.100 *
torr (mmHg, 0 °C)	pascal (Pa)	133.322
volt (int. of 1948)	volt (absolute) (V)	1.000 330
watt (int. of 1948)	watt (W)	1.000 165

* exact relationship to SI units.

In addition to the conversion factors for the specific units listed above the conversion factors for some frequently used compounded units derived from the specific units are listed below:

To convert from	to	Multiply by
	Compound Units	
	Heat	
Btu_{th}^{a}·in/(s·ft.^{2}·°F)	watt/metre-kelvin W/(m·°K)	518.873 2
Btu_{int}^{b}·in/(s·ft.^{2}·°F)	watt/metre-kelvin W/(m·°K)	519.220 4
Btu_{th}^{a}·in/(h·ft.^{2}·°F)	watt/metre-kelvin W/(m·°K)	0.144 131 4
Btu_{int}^{b}·in/(h·ft.^{2}·°F)	watt/metre-kelvin W/(m·°K)	0.144 272 9
Btu_{int}^{b}/ft^2	joule/metre^2 (J/m^2)	11 356.53
Btu_{th}^{a}/ft^2	joule/metre^2 (J/m^2)	11 348.93
Btu_{int}^{b}/(h·ft^2·°F)	watt/metre^2-kelvin W/(m^2·°K)	5.678 263
Btu_{th}^{a}/(h·ft^2·°F)	watt/metre^2-kelvin W/(m^2·°K)	5.674 466
Btu_{int}^{b}/pound-mass(lbm)	joule/kilogram (J/kg)	2 326.000 *
Btu_{th}^{a}/pound-mass(lbm)	joule/kilogram (J/kg)	2 324.444
Btu_{int}^{b}/(lbm·°F)	joule/kilogram-kelvin J/(kg·°K)	4 186.800 *
Btu_{th}^{a}/(lbm·°F)	joule/kilogram-kelvin J/(kg·°K)	4 184.000 *
cal_{th}^{a}/cm^2	joule/metre^2 (J/m^2)	41 840.000 *
cal_{th}^{a}/(cm^2·s)	watt/metre^2 (W/m^2)	41 840.000 *
cal_{int}^{b}/gram	joule/kilogram (J/kg)	4 186.800 *
cal_{th}^{a}/(cm·s·°C)	watt/metre-kelvin W/(m·°K)	418.400 *
cal_{th}^{a}/gram	joule/kilogram (J/kg)	4 184.000 *
cal_{int}^{b}/(gram·°C)	joule/kilogram-kelvin J/(kg·°K)	4 186.800 *
cal_{th}^{a}/(gram·°C)	joule/kilogram-kelvin J/(kg·°K)	4 184.000 *
	Mass/Volume	
gram/centimetre^3	kilogram/metre^3 (kg/m^3)	1 000.000 *
pound-mass/foot^3	kilogram/metre^3 (kg/m^3)	16.018 46
pound-mass/inch^3	kilogram/metre^3 (kg/m^3)	27 679.9
	Pressure	
atmosphere(normal) = 760 torr	pascal (Pa)	$1.013\ 25 \times 10^{5}$ *
atmosphere(tech.) = 1 kgf/cm^2	pascal (Pa)	$9.806\ 650 \times 10^{4}$ *
bar	pascal (Pa)	1.000×10^{5} *
centimetre of mercury (0°C)	pascal (Pa)	1 333.22
dyne/centimetre^2	pascal (Pa)	0.100 *
gram-force/centimetre^2	pascal (Pa)	98.066 500 *
kilogram-force/centimetre^2	pascal (Pa)	98 066.500 *
kilogram-force/metre^2	pascal (Pa)	9.806 650 *
kilogram/force/millimetre^2	pascal (Pa)	$9.806\ 650 \times 10^{6}$ *
poundal-foot^2	pascal (Pa)	1.488 164
pound-force/foot^2	pascal (Pa)	47.880. 26
pound-force/inch^2(psi)	pascal (Pa)	6 894.757
psi	pascal (Pa)	6 894.757
	Velocity	
foot/hour	metre/second (m/s)	$8.466\ 667 \times 10^{-5}$
foot/minute	metre/second (m/s)	5.080×10^{-3} *
foot/second	metre/second (m/s)	0.304 800 *
inch/second	metre/second (m/s)	0.025 400 *
kilometre/hour	metre/second (m/s)	0.277 778
mile/minute (U. S. statute)	metre/second (m/s)	26.822 400 *
	Viscosity	
foot^2/second	metre^2/second (m^2/s)	$9.290\ 304 \times 10^{-2}$ *
pound-mass/foot-second	pascal-second (Pa·s)	1.488 164
pound-force-second/foot^2	pascal-second (Pa·s)	47.880 26
	Volume	
foot^3	metre^3 (m^3)	$2.831\ 685 \times 10^{-2}$
inch^3	metre^3 (m^3)	$1.638\ 706 \times 10^{-5}$ *

[a] th = thermochemical; [b] Int = International Table

* exact relationship to SI units.

Some additional conversion data and other relevant data are shown below.

To convert	to	Multiply by
kJ/mol	J/mol	1 000
J/mol	kJ/kg	the reciprocal of the mass wt. in grams of 1 mole of substance
J/mol	J/kg	the reciprocal of the mass wt. in kg. of 1 mole of substance
J/(mol·°K)	kJ/(kg·°K)	the reciprocal of the mass wt. in grams of 1 mole of substance
J/(mol·°K)	J/(kg·°K)	the reciprocal of the mass wt. in kg of 1 mole of substance
J/(mol·°K)	cal/(mol·°C)	0.239 006
kg/m^3	lb/ft^3	0.062 428
kg/dm^3	lb/ft^3	62.428
kJ/mol	kcal/mol	0.239 006
J/mol	cal/mol	0.239 066
cm^3/kg	ft^{3}lb	0.016 018 463
kJ/kg	Btu/lb	0.430 210
dm^3	litre	1.000

To convert the SI unit to the corresponding non SI unit, *divide* the former by the appropriate multiplication factor or *multiply* by the reciprocal of the multiplication factor.

14.696 psia = 1 atm = 1.013 25 bar = 760 mmHg = 760 torr
= 101 325 pascals = 101.325 kPa = 101.325 kN/m2

SAFETY

Matheson has always emphasized safety. The chapter following the preface of this book is a treatise on the safe handling of compressed gases in the laboratory and plant.

The information presented in this Gas Data Book is in-

tended to convey the best available and most reliable data on gases in order to facilitate their safe handling and to stimulate their use. The uses referred to in this book are listed for illustrative purposes and it is suggested that sufficient investigation be conducted to establish the suitability of their application in any particular case. All statements, information, and data presented herein are believed to be accurate and reliable but no guarantee or warranty is implied or intended, nor can Matheson assume responsibility for any accidents or damages coincidental to their use including incidental or consequential damages. No statement or suggestion concerning the various gases implies immunity under any patents.

William Braker
Allen L. Mossman
1980

Acetylene	1
Air	11
Allene	17
Ammonia	23
Argon	34
Arsine	41
Boron Trichloride	45
Boron Trifluoride	50
Bromine Pentafluoride	56
Bromine Trifluoride	61
Bromotrifluoroethylene	66
Bromotrifluoromethane	70
1,3-Butadiene	79
Butane	88
1-Butene	97
2-Butene	105
Carbon Dioxide	120
Carbon Monoxide	130
Carbon Tetrafluoride	139
Carbonyl Fluoride	144
Carbonyl Sulfide	149
Chlorine	155
Chlorine Trifluoride	164
Chlorodifluoromethane	169
Chloropentafluoroethane	176
Chlorotrifluoroethylene	184
Chlorotrifluoromethane	189
Cyanogen	196
Cyanogen Chloride	202
Cyclobutane	206
Cyclopropane	209
Deuterium	215
Diborane	219
Dibromodifluoromethane	224
1,2-Dibromotetrafluoroethane	228
Dichlorodifluoromethane	231
Dichlorofluoromethane	239
Dichlorosilane	246
1,2-Dichlorotetrafluoroethane	251
1,1-Difluoro-1-Chloroethane	258
1,1-Difluoroethane	263
1,1-Difluoroethylene	269
Dimethylamine	274
Dimethyl Ether	280
2,2-Dimethylpropane	286
Ethane	292
Ethylacetylene	301
Ethyl Chloride	306
Ethylene	312
Ethylene Oxide	322
Fluorine	330
Fluoroform	336
Germane	341
Helium	344
Hexafluoroacetone	350
Hexafluoroethane	356
Hexafluoropropylene	362
Hydrogen	365
Hydrogen Bromide	372
Hydrogen Chloride	378
Hydrogen Cyanide	385
Hydrogen Fluoride	391
Hydrogen Iodine	398
Hydrogen Selenide	404
Hydrogen Sulfide	408
Iodine Pentafluoride	416
Isobutane	420
Isobutylene	430
Krypton	437
Methane	441
Methylacetylene	450
Methyl Bromide	456
3-Methyl-1-butene	462
Methyl Chloride	466
Menthyl Fluoride	476
Methyl Mercaptan	481
Methyl Vinyl Ether	487
Monoethylamine	492
Monomethylamine	498
Neon	504
Nickel Carbonyl	509
Nitric Oxide	514
Nitrogen	522
Nitrogen Dioxide	531
Nitrogen Trifluoride	538
Nitrogen Trioxide	543
Nitrosyl Chloride	545
Nitrous Oxide	550
Octofluorocyclobutane	557
Oxygen	562
Oxygen Difluoride	570
Ozone	574
Perchloryl Fluoride	578
Perfluorobutane	583
Perfluoro-2-Butene	586
Perfluoropropane	590
Phosgene	596
Phosphine	601
Phosphorous Pentafluoride	607
Phosphorous Trifluoride	611
Propane	615
Propylene	624
Silane	632
Silicon Tetrafluoride	636
Sulfur Dioxide	641
Sulfur Hexafluoride	649
Sulfur Tetrafluoride	655
Sulfuryl Fluoride	660
Tetrafluoroethylene	663
Tetrafluorohydrazine	667
Trichlorofluoromethane	670
1,1,2-Trichloro-1,2,2-Trifluoro-ethane	677
Trimethylamine	684
Vinyl Bromide	690
Vinyl Chloride	695
Vinyl Fluoride	701
Xenon	705

ACETYLENE

(Synonym: Ethyne)
(Formula: C_2H_2)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.026 038 kg
One Mole of C_2H_2	0.026 038 kg
Specific Volume @ 15.6 °C, 101.325 kPa	900.8 dm^3/kg; 14.43 ft^3/lb
Vapor Pressure @ 21.1 °C	4 479 kPa; 44.79 bar; 649.6 psia; 44.2 atm
Boiling Point @ 170 kPa	198.15 °K; −75.0 °C; −103.0 °F
Sublimation Point @ 101.325 kPa	189.15 °K; −84.0 °C; −119.2 °F
Triple Point	
Temperature	192.40 °K; −80.75 °C; −113.4 °F
Pressure	128 kPa; 1.28 bar
Absolute Density Gas @ 101.325 kPa @ 0.0 °C	1.174 7 kg/m^3
Relative Density Gas @ 101.325 kPa @ 0.0 °C (Air = 1)	0.908
Density Liquid @ −80.75 °C	0.610 kg/l
Critical Temperature	309.45 °K; 36.3 °C; 97.3 °F
Critical Pressure	6 242 kPa; 62.42 bar; 905.3 psia; 61.6 atm
Critical Volume	4.340 dm^3/kg
Critical Density	0.230 4 kg/dm^3
Critical Compressibility Factor	0.274
Latent Heat of Fusion @ −80.75 °C, 128 kPa	96.4 kJ/kg; 23.04 kcal/kg
Flammable Limits in Air	2.5–81% (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ 26.8 °C	
@ Constant Pressure	44.308 kJ/(kmol·°K); 44.308 J/(mol·°K) 10.590 cal/(mol·°C)
@ Constant Volume	35.915 kJ/(kmol·°K); 35.915 J/(mol·°K); 8.584 cal/(mol·°C)
Specific Heat Ratio, Gas @ 101.325 kPa @ 26.8 °C, Cp/Cv	1.234
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.010 0 mPa·s; 0.010 0 $mN·s/m^2$; 0.010 0 CP
Viscosity Liquid @ −80 °C	0.195 mPa·s; 0.195 $mN·s/m^2$; 0.195 CP
Thermal Conductivity, Gas @ 101.325 kPa @ 15.6 °C	0.020 06 W/(m·°K); 47.94 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −80 °C	18.8 mN/m; 18.8 dyn/cm
Solubility in Water @ 101.325 kPa (partial pressure of acetylene) @ 25 °C	0.94 cm^3/1 cm^3 water
Autoignition Temperature	679–713 °K; 406–440 °C; 763–824 °F
Heat of Combustion, Gas @ 25 °C and Constant Pressure Gross, to form H_2O (liq.) + CO_2 (gas)	1 299.6 kJ/mol., 310.62 kcal/mol
Net, to form H_2O (gas) + CO_2 (gas)	1 255.6 kJ/mol; 300.10 kcal/mol

Description

Acetylene is the simplest member of the class of unsaturated hydrocarbons called alkynes or acetylenes. It is one of the most important of all starting materials for organic synthesis, particularly in commercial operations. The usefulness of acetylene is partly due to the variety of addition reactions which its triple bond undergoes and partly due to the fact that its weakly acidic hydrogen atoms are replaceable by reaction with strong bases to form acetylide salts.

Pure acetylene is a colorless, highly flammable gas of agreeable ethereal odor. Acetylene of ordinary commercial purity has a distinctive garlic-like odor. It is very soluble in acetone, 1 volume of which will dissolve 300 volumes of acetylene at 1 207 kPa (175 psia). It is slightly lighter than air.

Acetylene is shipped dissolved in acetone. Acetylene cylinders are filled with a porous material which holds the acetone. Full cylinder pressure is 1 724 kPa (250 psig) at 21.1 °C (70 °F).

Specifications

Acetylene has a minimum purity of 99.6%. The chief impurity is air, about 0.03–0.3%. The acetone content of the gas depends on the cylinder temperature and pressure. Matheson purified acetylene is substantially free of phosphine, ammonia, and hydrogen sulfide, and is of the highest purity available commercially.

Uses

Because of its high chemical reactivity, acetylene is an extremely versatile chemical in industrial syntheses. Approximately 85% of the annual acetylene production of the United States is used for chemical synthesis. Acetylene has come into increasing prominence as the raw material for a whole series of organic compounds, among them vinyl chloride, neoprene, vinyl acetate, acrylonitrile, vinyl ethers, vinylacetylene, trichloroethylene, and perchloroethylene (2).

The remaining 15% of the acetylene production is principally used for oxyacetylene cutting, heat-treating, etc., and as fuel for atomic absorption instruments.

Toxicity

Acetylene is a simple asphyxiant and anesthetic. Inhalation of 100,000 ppm (10%) acetylene has a slight intoxicating effect in man. Marked intoxication occurs at 200,000 ppm (20%), loss of coordination at 300,000 ppm (30%), and unconsciousness (upon 5 minutes of exposure) at 350,000 ppm (35%). No evidence exists that repeated exposure to tolerable levels of acetylene has any deleterious effects on health. The maximum permissible limit for acetylene in a working environment should not exceed 5000 ppm (0.5%). No threshold limit value has been recommended for acetylene because the limiting factor is the available oxygen.

First Aid

Exposure to high concentrations of acetylene causes intoxication and loss of coordination. Workers with these symptoms should be removed at once to uncontaminated air and a physician should be called. If the exposure was severe enough to cause loss of consciousness, oxygen should be administered. If breathing has stopped, start artificial respiration immediately and call a physician at once.

Precautions in Handling and Storage

1. Acetylene, in its free state under pressure, may decompose violently. The higher the pressure, the smaller the initial force required to cause an explosion. Therefore, *NEVER* use the free gas outside the cylinder at pressures in excess of 103 kPa (15 psig). Pressures exceeding this limit are utilized for chemical synthesis; however, special means to ensure safety are employed.
2. When using acetylene, close the cylinder valve before shutting off the regulator, to permit the gas to bleed from the regulator.
3. Acetylene cylinders should be used or stored only in an upright position to avoid the possibility of acetone leaking from the cylinder.
4. Never store reserve stocks of acetylene cylinders with reserve stocks of cylinders containing oxygen. They should be separately grouped.
5. Acetylene is highly flammable. Do not store acetylene cylinders near an open flame, nor where, in case of a leak, the gas can diffuse to a flame or spark from a motor.
6. When using acetylene, good ventilation should always be provided to remove any explosive mixture as rapidly as possible.
7. When returning empty acetylene cylinders, see that valves are closed to prevent evaporation of the acetone.
8. There are rigid regulations covering the filling of acetylene cylinders and since this process may be hazardous if improperly done, acetylene cylinders must be filled only by experts in plants manufacturing the gas.
9. It is preferable that acetylene be stored in an upright position; however, where this is impossible, it is recommended that the cylinder be put in an upright position and left that way for about a half hour before being used.
10. When installing acetylene cylinders, the user should comply with all local, state, and municipal regulations, and with the standards of the National Fire Protection Association (3).

For general handling instructions see Appendix I.

Leak Detection and Control

Never use a flame to detect acetylene leaks. Acetylene leaks may be detected by painting suspected areas with soap water; leaks will be evident by bubble formation.

Disposal of Leaking Cylinders

Consult Appendix II-A for appropriate procedure for disposal.

Analytical Detection

Slight traces of acetylene in the atmosphere can be detected by the Ilosvay test.

The Ilosvay reagent is prepared by dissolving 0.001 kg of cupric nitrate, $Cu(NO_3)_2 \cdot 5H_2O$, or the chloride or sulfate, in distilled water in a 50 ml volumetric flask. Four ml of concentrated ammonium hydroxide and 0.003 kg of hydroxylamine hydrochloride are added. The mixture is shaken until colorless and made up to volume. Covering the reagent with mineral oil or adding some copper wire will prolong the activity of the reagent.

About 10 ml of the reagent is placed in a glass-stoppered cylinder or separatory funnel and a collected volume of the atmosphere passed in, and the solution shaken. The presence of acetylene is indicated by the formation of a pink or red color due to formation of copper acetylide.

Matheson has available a manually operated "Toxic Gas Detector" Model 8014K which provides accurate, dependable and reproducible results in determining concentrations of acetylene in the range of 50 to 1000 ppm in air. The detector tube used is the Model 8014-101 S. A color stain is produced which varies in length according to the concentration of the acetylene present. The acetylene concentration is then read directly from the tube's scale.

Matheson

Fire Prevention and Control

Carelessness in welding and burning operations have caused accidents with the use of acetylene cylinders. Flames and molten metal can cause the fuse metal used as safety devices in cylinders of acetylene to melt, causing the acetylene to escape and possibly ignite. Care should be taken to see that acetylene cylinders are located as far as possible from falling molten metal and slag. Torches should be directed away from the area of the cylinder.

Small fires caused by ignited acetylene leaks can frequently be extinguished by smothering with a heavy cloth, wet waste, or piece of putty slapped at the leaking part (3). If the flame is issuing from the valve outlet, it may be possible to close the valve and stop the source of escaping gas. In all cases of acetylene cylinder fires, the area should be evacuated as quickly as possible and someone experienced in handling such a situation should take charge.

Literature is available for fire prevention around welding operations and the handling of burning acetylene cylinders (4).

Materials of Construction

Steel and wrought iron are recommended for use with acetylene. Joints may be welded or made of threaded or flanged fittings. Rolled, forged, or cast steel, or malleable iron fittings may be used. The use of cast iron fittings is not permissible.

Unalloyed copper, silver, and mercury should never be used in direct contact with acetylene due to the possible formation of explosive acetylides.

Wet acetylene produces explosive acetylides on copper, 70-30 brass and aluminum-bronze, the rate of formation being increased by the presence of air or carbon dioxide. The acetylide is formed much less rapidly on the brass and is less sensitive.

Explosive copper acetylides may be formed on copper and brasses down to 50% of copper when exposed to acetylene atmospheres under certain conditions where the metals have been contaminated with certain common acids and caustic soda. The article by Brameld, **et al** (5) should be consulted for detailed information on the formation of acetylides.

Cylinder and Valve Description

The acetylene cylinder contains a highly porous monolithic filler on which the acetone is absorbed. The acetylene is dissolved in the acetone, and in this state may be shipped at a pressure of 1 724 kPa (250 psig) at 21.1 °C (70 °F). The valve outlet designated as standard for acetylene by the Compressed Gas Association (CGA) has a thread size of 0.885 inch i.d.-14 threads per inch and is left-hand with internal threads, accepting a bullet-shaped nipple. It is designated as value outlet No. 510. This valve outlet and its mating connection are illustrated in Figure 1.

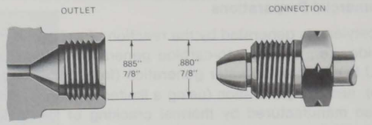


Fig. 1. CONNECTION 510 .885"-14 LH INT. accepting a Bullet Shaped Nipple

Safety Devices

Safety devices used on acetylene cylinders contain a fusible metal that melts at about 100 °C (212 °F). In large cylinders, these devices are usually in the form of plugs. Safety devices in small cylinders usually consist either of small plugs incorporated in the cylinder valve or a passage in the valve body filled with the fusible metal.

Recommended Controls

Automatic Pressure Regulators

Since the pressure of acetylene must be closely controlled, the only type of recommended control is an automatic pressure regulator. Matheson supplies an automatic single stage regulator Model 1PA-510. This regulator is of forged brass and is equipped with a delivery pressure gauge and tank gauge. A needle valve is provided at the regulator outlet for accurately controlled flow. This regulator will permit setting of accurate delivery pressures from 13.8–103 kPa (2–15 psig).

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Acetylene is shipped under Department of Transportation (DOT) regulations as a flammable, compressed gas, taking a DOT "Red Gas Label". It is shipped in DOT specifications DOT-8 or DOT-8A1 cylinders. The DOT regulates the amounts of acetone and acetylene that may be charged into a cylinder. These regulations specify the cylinder pressure to be no higher than 1 724 kPa (250 psig) at 21.1 °C (70 °F) when the cylinder is full.

Matheson

Commercial Preparations

Acetylene is generated by the reaction of water and calcium carbide, i.e., by water-to-carbide generation (widely used in the U.S.), carbide-to-water generation (frequently used in Europe), and dry generation (using a limited amount of water). It is also manufactured by thermal cracking of low-molecular-weight aliphatic hydrocarbons and by partial oxidation of natural gas or other methane-rich feedstock with a limited amount of oxygen, an amount insufficient for complete combustion. Details of these processes are described in Reference 6.

Chemical Properties

1. Acetylene, because of its triple bond, reacts additively with a wide variety of reagents, e.g., hydrogen, halogens, hydrogen halides, hydrogen cyanide, alcohols, carboxylic acids, aliphatic amines, arsenic trichloride and others.

2. Either one or both of the hydrogen atoms in acetylene are replaceable by certain metals to form acetylides. The acetylides are highly explosive when dry and reconverted to acetylene on treatment with water or dilute mineral acids. Acetylene when passed into a liquid ammonia solution of sodium amide (formed *in situ*) yields monosodium acetylide. The calcium, lithium, potassium, and barium derivatives have been similarly prepared. Copper, silver, and mercury acetylides are formed by passing acetylene into ammoniacal solutions of their salts. Interaction of acetylene with a Grignard reagent (RM_gX) in an inert solvent normally gives the dimagnesium halide ($XM_gC{:}CM_gX$), but the monomagnesium halide ($HC{:}CM_gX$), can be prepared under carefully controlled conditions.

3. Treatment of acetylene with a cuprous ammonium chloride catalyst results in self-addition; vinylacetylene is formed. When acetylene is heated in the presence of a nickel catalyst in tetrahydrofuran (60–70 °C and 10–25 atm), cyclooctatetraene is formed in 75–85% yield.

4. Acetylene can be added to the double bond of the carbonyl group in the presence of appropriate catalysts (ethynylation). Thus, formaldehyde reacts with acetylene diluted with an inert gas at about 100 °C and 3 atm or higher in the presence of wet supported cuprous acetylide as catalyst to give the mono-addition product propargyl alcohol and the di-addition product 2-butyne-1,4-diol. Ketones react with acetylene in ethyl ether, acetal, or polyethers as solvents in the presence of sodium or potassium hydroxide, sodamide, potassium tert-butoxide, or other alkali or alkaline earth oxides as condensing agents. Thus, acetone and 2-butanone give 2-methyl-3-butyn-2-ol and 3-methyl-1-pentyn-3-ol, respectively.

5. Acetylene adds water directly when treated with hot dilute sulfuric acid in the presence of some mercuric sulfate and forms acetaldehyde.

6. The catalyzed reaction of acetylene with carbon monoxide and an aliphatic alcohol gives an acrylic acid ester (7); the reaction with water gives acrylic acid.

7. Diazomethane reacts with acetylene to form pyrazole.

8. When acetylene and hydrogen sulfide are passed over alumina at 425–450 °C thiophene is formed together with other by-products.

9. Reaction of alcohols, including polyols and phenols, with acetylene under pressure at 120–180 °C in the presence of alkaline catalysts gives vinyl ethers.

10. Reaction of acetylene and hydrogen chloride in the vapor phase at 150–250 °C in the presence of a contact catalyst, such as mercuric chloride on charcoal, gives vinyl chloride.

11. Acetic acid adds to acetylene in the vapor phase at 180–200 °C over a contact catalyst, such as cadminum, zinc, or mercury salts deposited on charcoal, to give vinyl acetate.

12. Hydrogen cyanide adds to acetylene in the vapor or liquid phase to give acrylonitrile.

13. Secondary aromatic amines, such as carbazole and diphenylamine, react with acetylene under pressure at 150–200 °C in the presence of alkali, zinc, or cadmium oxides, or their salts with organic acids, to give the corresponding N-vinyl derivatives.

14. Passage of acetylene through an aqueous solution of cuprous chloride, ammonium chloride, and hydrogen chloride at 50–60 °C in the absence of oxygen or in the presence of antioxidants gives vinylacetylene together with divinylacetylene.

15. Acetylene can be copolymerized in tetrahydrofuran at 60–70 °C and 10–25 atm of acetylene pressure in the presence of anhydrous nickel cyanide as catalyst to cyclooctatetraene, along with other products.

16. Acetylene burns in air with a high flame temperature, variously reported between 2982–3482 °C (5400 and 6300 °F).

Thermodynamic and Detailed Physical Data

Molecular Structure

Acetylene has been established by various physical measurements to be a linear molecule, point group $D_{\infty h}$, with a C:C bond distance of 1.20×10^{-10} m (1.20 Å) and two C—H bond distances of 1.06×10^{-10} m (1.06 Å). In acetylene the C—H bonds are σ bonds formed by the overlap of a hydrogen s orbital with a carbon sp orbital; there is one C—C σ bond from overlap of two carbon sp orbitals and there are two C—C π bonds from overlap of two perpendicular pairs of p orbitals. This formulation fits well with the properties of acetylene bonds in being linear with high chemical reactivity (π bonds exposed) (8).

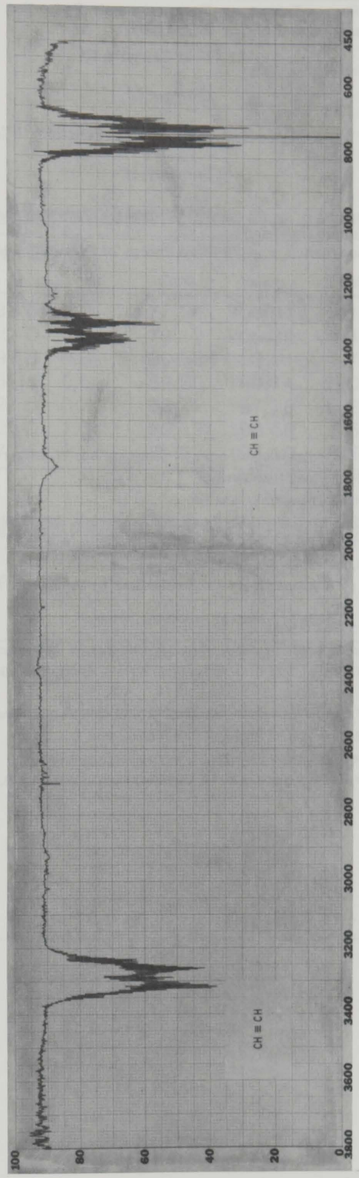
Infrared Spectrum

See Figure 2 for infrared spectrum of gaseous acetylene.

Vapor Pressure (9)

Vapor pressures below 101.325 kPa (1 atm) are listed below.

Temperature, °C	Vapor Pressure kPa	mbar	mmHg torr
−142.9	0.133 3	1.333	1
−133.0	0.666 6	6.666	5
−128.2	1.333	13.33	10
−122.8	2.666	26.66	20
−116.7	5.333	53.33	40
−112.8	7.999	79.99	60
−107.9	13.33	133.3	100
−100.3	26.66	266.6	200
−92.0	53.33	533.3	400
−84.0	101.325	1 013.25	760



Reprinted through the courtesy of Sadtler Research Laboratories
© Sadtler 1972

Fig. 2. High resolution infrared spectrum of gaseous acetylene over the frequency range 3 800–450 cm^{-1}; path length: 10 cm; KBr windows; pressure: 2.666 kPa (20 mmHg) (1:1).

Matheson

For other vapor pressures below 101.325 kPa, see Table 1.

For vapor pressures above 101.325 kPa, see Table 2 and Figure 3.

For vapor pressure of acetylene in acetone solution, see Figure 4.

See Table 2 for latent heats of vaporization.

Thermodynamic Data

For the thermodynamic properties of the saturated liquid and vapor, see Table 2. See Table 3 for the thermodynamic properties of superheated acetylene.

Thermodynamic Properties of Acetylene As Ideal Gas @ 25 °C (10)

Heat Capacity, C_p°	44.095 J/(mol·°K) 10.539 cal/(mol·°C)
Entropy, S°	200.848 J/(mol·°K) 48.004 cal/(mol·°C)
Free Energy Function, $(F^\circ_{298} - H^\circ_{298})/T$	−200.848 J/(mol·°K) −48.004 cal/(mol·°C)
Enthalpy, H°	10.012 kJ/mol 2 393.9 cal/mol
Enthalpy of Formation, ΔH_f°	226.731 kJ/mol 54.190 kcal/mol
Free Energy of Formation, ΔF_f°	209.171 kJ/mol 49.993 kcal/mol

REFERENCES

[1] For the extensive tabulation of the physical and thermodynamic properties of acetylene, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] *Acetylene*, Pamphlet G-1, Compressed Gas Association, New York, New York.

[3] *Gas Systems for Welding and Cutting*, NFPA Standard 51, National Fire Protection Association, Boston, Massachusetts.

[4] *Recommended Safe Practice in Cutting and Welding*, Air Reduction Company, New York, New York.

[5] Brameld, Clark, and Seyfang, *J. Soc. Chem. Ind.* (London) 66, 346–353 (1947).

[6] H. Beller and J. M. Wilkinson, Jr., in Kirk-Othmer's *Encyclopedia of Chemical Technology*, 2nd edition, *1963*, Volume 1, pp. 174–193, John Wiley & Sons, Inc. New York, New York.

[7] F. Sakakibra, *J. Soc. Org. Synth. Chem.* (Japan) 23, 757 (1965).

[8] J. D. Roberts and M. C. Caserio, *Basic Principles of Organic Chemistry*, *1964*, pp. 139, 209, W. A. Benjamin, Inc., New York, New York.

[9] *Chemical Engineers' Handbook*, R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, editors, 4th edition, *1963*, p. 3–47, McGraw-Hill Book Co., New York, New York.

[10] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, National Standard Reference Data Service, National Bureau of Standards, NARDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[11] *The Sadtler Standard Spectra*, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[12] *Thermodynamic Functions of Gases*, F. Din, editor, *1962*, Volume 2, p. 77, Butterworth, Inc., Washington, D. C.

[13] **Ibid.**, pp. 78–79.

[14] **Ibid.**, pp. 80–81.

[15] **Ibid.**, pp. 86–87.

Table 1. THERMODYNAMIC PROPERTIES OF THE SATURATED SOLID AND VAPOR (12)

Temperature, °K	Pressure kPa	Pressure atm	Entropy J/(mol·°K) Solid	Entropy J/(mol·°K) Vapor	Enthalpy kJ/mol Solid	Enthalpy kJ/mol Vapor	Specific Volume cm^3/mol Solid	Specific Volume cm^3/mol Vapor
161.96	10.132 5	0.1	77.24	209.91	4.121	25.606		132 300
169.27	20.265 0	0.2	79.12	205.39	4.498	25.870		68 850
173.88	30.397 5	0.3	80.58	203.01	4.736	26.020		46 990
180.04	50.662 5	0.5	82.30	199.74	5.063	26.209		29 060
184.34	70.927 5	0.7	83.72	197.78	5.297	26.321		21 100
189.13	101.325 0	1.0	85.19	195.56	5.565	26.439	35.7	15 050
192.4 (T.P.)	128.277 5	1.266	86.23	194.10	5.753	26.506		12 020

Table 2. THERMODYNAMIC PROPERTIES OF THE SATURATED LIQUID AND VAPOR (12)

Temperature °K	Temperature °F	Pressure kPa	Pressure atm	Entropy J/(mol·°K) Liquid	Entropy J/(mol·°K) Vapor	Enthalpy kJ/mol Liquid	Enthalpy kJ/mol Vapor	Latent Heat of Vaporization kJ/mol	Specific Volume cm^3/mol Liquid	Specific Volume cm^3/mol Vapor	Density kg/dm^3 Liquid	Density kg/dm^3 Vapor
192.4 (T.P.)	−113.35	128.277	1.266	107.45	194.10	9.832	26.506	16.674	42.7	12 020	0.610	0.002 17
200.9	−98.05	202.650	2	111.84	191.67	10.707	26.744	16.037	43.0	7 840	0.606	0.003 32
209.4	−82.75	303.975	3	116.15	189.54	11.590	26.959	15.368	43.9	5 400	0.593	0.004 82
221.5	−60.97	506.625	5	121.96	186.94	12.832	27.225	14.393	45.4	3 290	0.574	0.007 91
230.4	−44.95	709.275	7	125.94	185.14	13.753	27.393	13.640	46.7	2 361	0.558	0.011 07
240.7	−26.41	1 013.250	10	129.91	183.22	14.715	27.547	12.832	48.4	1 654	0.538	0.015 7
253.2	−3.91	1 519.875	15	133.64	180.87	15.673	27.635	11.962	50.9	1 093	0.512	0.023 8
263.0	13.73	2 026.500	20	136.19	179.08	16.351	27.631	11.280	53.2	804	0.489	0.032 4
271.6	29.21	2 533.125	25	138.66	177.61	17.016	27.593	10.577	55.5	626	0.469	0.041 6
278.9	42.35	3 039.750	30	140.96	176.19	17.694	27.514	9.820	58.0	503	0.449	0.051 8
284.9	53.15	3 546.375	35	143.05	174.85	18.318	27.376	9.058	60.3	414	0.432	0.062 9
290.4	63.05	4 053.000	40	145.18	173.34	18.933	27.112	8.179	62.9	345	0.414	0.075 5
300.0	80.33	5 066.250	50	149.37	170.12	20.251	26.476	6.225	70.2	243	0.371	0.107 2
307.8	94.37	6 079.500	60	155.31	165.35	22.121	25.209	3.088	87.3	159	0.298	0.163 8
308.7	95.99	6 246.686	61.65	160.33		23.644		0.000	112.9		0.230 6	

Table 3. THERMODYNAMIC PROPERTIES OF SUPERHEATED ACETYLENE

H, ENTHALPY, (13), kJ/mol; **S**, ENTROPY (14), J/(mol·°K); **V**, SPECIFIC VOLUME (15), cm^3/mol

Pressure kPa	Bar	atm		Temperature, °K 160	180	200	220	240	260	280	300	310	320
			H	25.556*	26.237	26.977	27.709	28.492	29.303	30.142	31.077	31.450	31.899
10.132 5	0.101	0.1	S	209.45*	211.49	217.24	220.83	224.240	227.48	230.59	233.56	235.02	236.44
			V	130 700*	147 200	163 700	180 200	196 700	213 100	229 500	245 900	254 100	262 300
			H		26.174	26.906	27.667	28.458	29.273	30.117	30.985	31.429	31.879
50.662 5	0.507	0.5	S		199.87	203.71	207.33	210.77	214.04	217.15	220.15	221.15	223.03
			V		29 050	32 410	35 770	39 110	42 430	45 750	49 050	50 700	52 350
			H	25.371*	26.094*	26.842	27.616	28.414	29.236	30.084	30.957	31.403	31.855
101.325	1.013 2	1	S	189.53*	193.79*	197.73	201.41	204.88	208.17	211.32	214.33	215.79	217.22
			V	12 460*	14 250*	16 000	17 720	19 410	21 100	22 780	24 450	25 280	26 100
			H				27.159*	28.043	28.928	29.822	30.731	31.193	31.659
506.625	5.066	5	S				186.60*	190.44	193.99	197.30	200.43	201.94	203.42
			V				3 250*	3 647	4 024	4 389	4 747	4 923	5 098
			H					27.511*	28.503	29.472	30.436	30.919	31.405
1 013.250	10.13	10	S					183.11*	187.07	190.66	193.98	195.57	197.31
			V					1 657*	1 879	2 086	2 282	2 377	2 470
			H						28.020	29.091	30.122	30.631	31.140
1 519.875	15.20	15	S						182.36	186.33	189.87	191.55	193.17
			V						1 154	1 313	1 457	1 526	1 594
			H						27.440*	28.669	29.787	30.328	30.862
2 026.500	20.26	20	S						178.28*	182.83	186.69	188.46	190.16
			V						779.0*	921.5	1 043	1 099	1 153
			H							28.182	29.423	30.006	30.570
2 533.125	25.33	25	S							179.67	183.95	185.85	187.64
			V							679.5	791.2	841.0	888.2
			H							27.598	29.024	29.656	30.261
3 039.750	30.40	30	S							176.50	181.43	183.51	185.43
			V							510.9	620.8	667.3	710.3
			H								28.060	28.861	29.579
4 053.000	40.53	40	S								176.52	179.15	181.44
			V								399.0	445.1	485.2
			H								26.475	27.835	28.774
5 066.250	50.66	50	S								170.17	174.63	177.62
			V								239.7	302.7	345.4
			H									26.109	27.757
6 079.500	60.80	60	S									168.27	173.51
			V									185.9	246.4
			H									20.822	23.974
8 106.000	81.06	80	S									150.65	160.64
			V									62.3	99.9
			H									19.947	22.021
10 132.500	101.32	100	S									147.46	154.06
			V									53.0	67.4

* Supersaturated

FIG. 3
ACETYLENE
(pure)
VAPOR PRESSURE vs TEMPERATURE

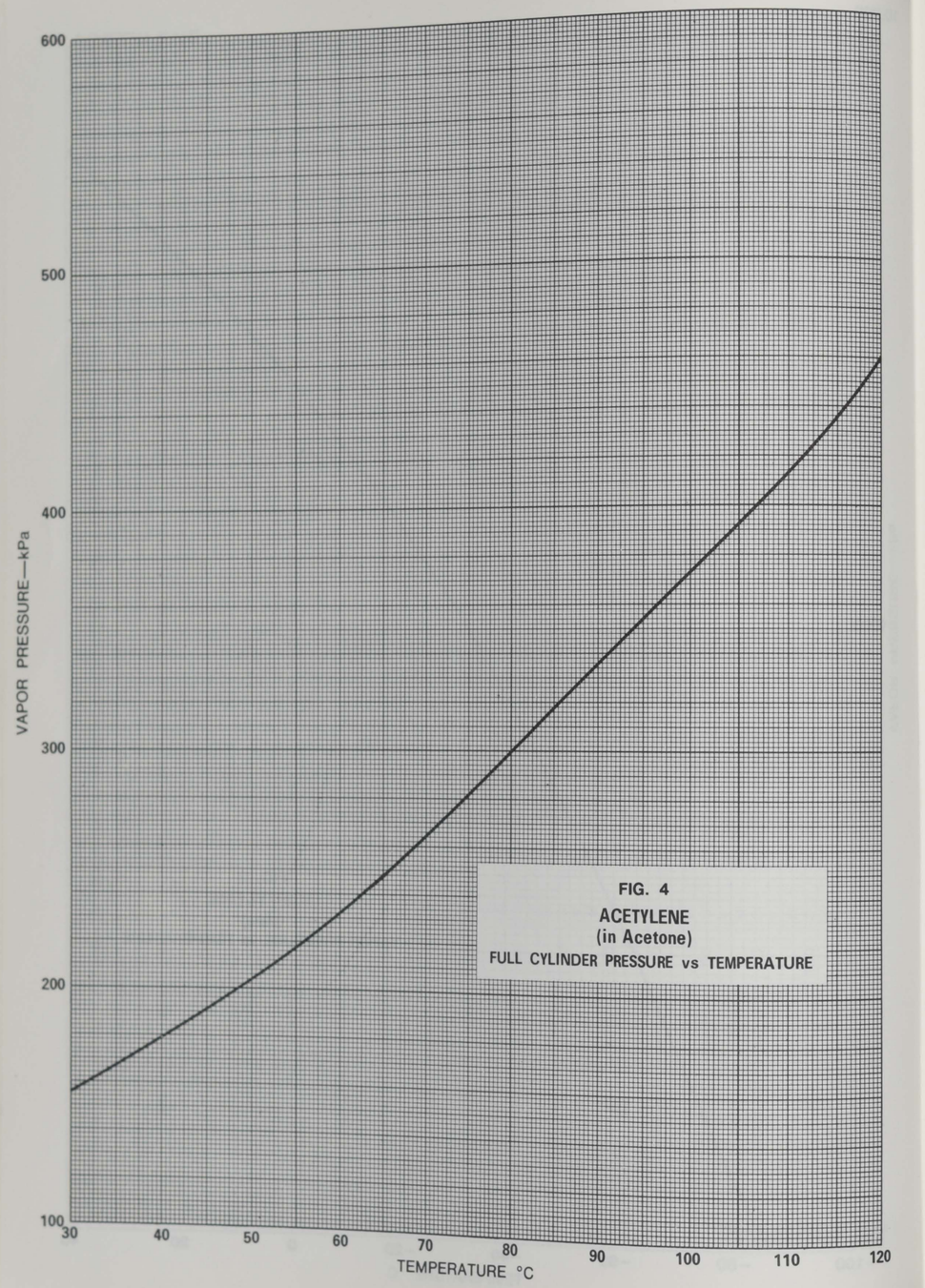


FIG. 4
ACETYLENE
(in Acetone)
FULL CYLINDER PRESSURE vs TEMPERATURE

PHYSICAL PROPERTIES (1)

Mean Molar Mass	
Mean Molecular Weight	0.028 96 kg
One Mole of Air	0.028 96 kg
Specific Volume @ 21.1 °C, 101.325 kPa	830.3 dm^3/kg; 13.3 ft^3/lb
Boiling Point of Liquid @ 101.325 kPa (Bubble Point) (2)	78.8 °K −194.35 °C; −317.8 °F
Condensation Point of Vapor @ 101.325 kPa (Dew Point)	81.8 °K; −191.35 °C; −312.4 °F
Absolute Density, Dry Air @ 101.325 kPa @ 0 °C	1.293 1 kg/m^3
Density Liquid Air	
For liquid densities under saturation pressure, see Table 1.	
Critical Constants (2)	
@ Plait Point:	
Temperature	132.42 °K; −140.6 °C; −221.3 °F
Pressure (maximum)	3 774 kPa; 37.74 bar; 547.4 psia; 37.25 atm
Volume	3.048 dm^3/kg
Density	0.328 kg/dm^3
@ Point of Contact:	
Temperature (maximum)	132.52 °K; −140.6 °C; −221.1 °F
Pressure	3 766 kPa; 37.66 bar; 546.2 psia; 37.17 atm
Volume	3.126 dm^3/kg
Density	0.320 kg/dm^3
Molar Specific Heat, Gas @ 101.325 kPa @ 26.85 °C	
@ Constant Pressure	29.13 kJ/(kmol·°K); 29.13 J/(mol·°K); 0.240 Btu/(lb·°F)
Constant Volume	20.8 kJ/(kmol·°K); 20.8 J/(mol·°K); 0.172 Btu/lb·°F
Specific Heat Ratio, Gas @ 101.325 kPa, @ 26.85 °C	
Cp/Cv	1.400
Viscosity, Gas @ 101.325 kPa, @ 26.85 °C	0.018 53 mPa·s; 0.018 53 $mN·s/m^2$; 0.018 53 cP
(For viscosity vs. temperature curve, see Figure 1.)	
Viscosity, Liquid @ −192.3 °C	0.172 mPa·S; 0.172 $mN·s/m^2$; 0.172 cP
Thermal Conductivity, Gas @ 101.325 kPa, @ 26.85 °C	0.027 79 W/(m·°K); 62.72 × 10^{-6} cal·cm/(s·cm^2 °C)
Solubility In Water @ 101.325 kPa (partial pressure of air) @ 20 °C	18.68 cm^3 air/l water

Description

Air is a mixture, the composition of which varies with the altitude at which the sample is taken, i.e., its composition begins to change materially above 62 miles. It is shipped in steel cylinders generally at 15 170 kPa (2 200 psig) and 13 790 kPa (2 000 psig), and in lecture bottles at 12 240 kPa (1 775 psig) at 21.1 °C.

The average composition of dry air at surface altitudes is shown in Table 1.

Since air is a mixture, there are two vapor pressure curves, one for the saturated liquid and the other for the saturated

Table 1

Component	Mole %	Weight %
Nitrogen	78.084	75.521
Oxygen	20.946	23.139
Argon	0.934	1.288
Carbon Dioxide	0.033	0.050
Rare Gases	0.003	0.002

The average composition of rare gases in dry air is shown in Table 2.

vapor, corresponding with the bubble and dew points. The essential feature of the dew and bubble points of air is that one phase should predominate (liquid at the bubble point, vapor at the dew point) with the other phase being present theoretically in infinitesimally small quantity. In addition, the phenomenon of retrograde condensation associated with mixtures at the critical point is observed and values are obtained for the two critical points, the so-called plait point where the pressure is a maximum and the point of contact where the temperature is a maximum.

Table 2 does not show water vapor, ozone, oxides of nitrogen, acetylene, methane and other hydrocarbons, and other highly variable components of the air. Except for water vapor, these components are usually present only in trace quantities or not at all.

Table 2

Component	PPM (By Volume)	PPM (By Weight)
Neon	18.18 ± 0.04	12.67
Helium	5.239 ± 0.004	0.724
Krypton	1.139 ± 0.01	3.295
Hydrogen	0.5	0.035
Xenon	0.086 ± 0.001	0.390
Radon	6×10^{-14}	46×10^{-14}

VAPOR PRESSURE—kPa

Specifications

Matheson offers several grades of air. These grades and their specifications are shown below.

Grade	Specifications
Air, Ultra Zero	Total hydrocarbons less than 0.1 ppm as CH_4
Air, Emission Zero	Total hydrocarbons 1 ppm max, CO 1 ppm max, CO_2 300 ppm max
Air, Zero Gas	Total hydrocarbons less than 2.0 ppm as CH_4
Air, CO_2 Free	Total CO_2 equivalent less than 5 ppm
Air, Dry	Dew Point −59.4 °C (−75 °F) max

Uses

Air is a source of oxygen, nitrogen and rare gases. Liquid air is used for low temperature cooling operations, while atmospheric air is used in air conditioning systems or cooling of hot liquids in heat exchangers. Air is the source of oxygen for burning, respiration of plants and animals, decay, and industrial oxidations. Zero grade air is regularly used as the oxidizer for flame ionization detectors in chromatography and total hydrocarbon analyzers.

Precautions in Handling and Storage

The general rules stated in Appendix I should be observed.

Materials of Construction

Since dry air is inert to metals and plastics at ambient temperatures, no special materials of construction are required. However, any piping or vessels containing dry air should be adequately designed by competent engineers, using a safety factor conforming with the ASME code for pressure piping.

Cylinder and Valve Description

Dry air is packaged in DOT approved, high pressure steel cylinders which contain Compressed Gas Association (CGA) cylinder valve outlet connection No. 590 (see Figure 1). The

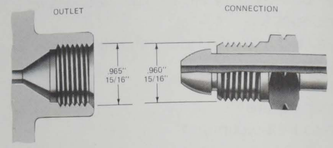


Fig. 1. CONNECTION 590 .965"-14 LH INT. accepting a Bullet Shaped Nipple

cylinder valve outlet has a 0.965 inch diameter internal thread, left hand, accepting a bullet-shaped nipple. Lecture bottles have a special dual valve 9/16"-18 R.H. male and 5/16"-32 female.

Safety Devices

Cylinders containing dry air have safety devices of either the frangible disc type or frangible disc backed up with fusible metal, melting at approximately 100 °C (212 °F). These safety devices are in an integral part of the cylinder valve, situated opposite the valve outlet.

Recommended Controls

Automatic Pressure Regulators

In order to reduce the high cylinder pressure of air to a safe working value consistent with a system's design, the following types of controls are recommended.

1. Single Stage Automatic Regulators

Single stage regulators will reduce cylinder pressure in one stage to a delivery pressure in a particular range, depending upon the design of the regulator and its spring load. A single stage regulator will show a slight variation in delivery pressure as cylinder pressure falls. The following single stage regulators are available from Matheson:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
19-590	28–345	0.28–3.45	4–50
3500-590	28–520	0.28–5.2	4–75
1L-590	28–550	0.28–5.5	4–80
1H-590	69–1 240	0.69–12.4	10–180
2-590	345–4 480	3.45–44.8	50–650
3-590	690–10 340	6.9–103.4	100–1 500
4-590	690–17 240	6.9–172.4	100–2 500

2. Two Stage Regulators

This type of regulator performs the same function as a single stage regulator. However, greater accuracy and control of the delivery pressure is maintained and the delivery pressure does not vary as cylinder pressure falls. The following two stage regulators are available from Matheson:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
3800-590	28–620	0.28–6.2	4–90
3104-590	28–690	0.28–6.9	4–100
8L-590	14–104	0.14–1.04	2–15
8-590	28–340	0.28–3.4	4–50
8H-590	69–690	0.69–6.9	10–100
9-590	138–1 720	1.38–17.2	20–250

3. Low-Pressure Regulators

The above regulators are not satisfactory for accurate delivery pressures below 34.5 kPa (5 psig). Therefore, an auxilary regulator specifically designed for low pressure is recommended for use in series with any of the above standard type regulators having delivery pressures to 345 kPa (50 psig). Matheson has various models known as the Model 70 regulators which may be obtained with delivery pressures ranging from 0.5 kPa to 69 kPa (10 psig) as follows:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
70B	0.5–3.0	0.005–0.030	2–12 inches water column
70	3.4–34.5	0.034–0.345	0.5–5 psig
70A	34.5–69	0.345–0.69	5–10 psig

For air, the Model 70 regulator may be used in series with the Model 1L-590 regulator; inlet pressure must not exceed 1724 kPa (250 psig) to obtain a delivery pressure of 3.4–34.5 kPa (0.5–5 psig).

Manual Controls

Manual needle valves for direct attachment to the cylinder valve outlet are available. These types of controls are mainly used where intermittent flows are necessary, or where it is desired to control the flow of gas directly from the cylinder. This type of needle valve will allow control of extremely low flow rates on up to relatively large flow rates. However, pressure cannot be controlled with such a valve, and if a line or system becomes plugged, dangerous pressures can build up. Matheson manual needle valves Model 50-590 and Model 52-590 with gauge to indicate tank pressure are recommended for use with dry air. These valve are normally supplied with serrated hose ends, ¼" compression fittings, or ¼" NPT male or female outlets. Manual control valve Model 4351-590 is recommended for use with all grades of air, except the Dry Air Grade.

For lecture bottles, regulator Model 3320 is recommended as well as the control valves Model 30AR or Model 31B.

Flowmeters

In all cases where accurate flows of a definite value must be known or reproduced, it is recommended that a suitable flowmeter of the rotameter type, such as Matheson Series 7600 flowmeter units with 150 mm tubes and floats or the 7200 Series flowmeter units with 65 mm tubes with a single float be used. For dry air, flowmeters of brass construction are recommended, while for all other grades of air, flowmeters of brass or stainless steel construction may be used.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Dry air is shipped in high pressure steel cylinders as a nonflammable compressed gas, taking a DOT "Green Label."

Commercial Preparations

Dry air is produced from ordinary air by first removing the hydrocarbons by oxidation, then removing the carbon dioxide, compressing and drying.

Chemical Reactions

Liquid air is a source of nitrogen, oxygen, neon, argon, krypton, and xenon. These gases are obtained from liquid air by complex fractionation and rectification processes.

The reactivity of air is due to its content of oxygen. Many metals are converted to oxides when they are heated in air. In organic chemistry, the oxygen in the air, while the cheapest oxidizer, is relatively unselective and is seldom used in chemical syntheses in the laboratory. However, a number of chemicals are produced industrially by oxidation with air frequently using catalysts and moderately elevated temperatures. These processes include the liquid phase of oxidation of acetaldehyde or ethanol to acetic acid, the formation of a hydroperoxide from a saturated hydrocarbon, the catalytic oxidation of methanol vapor to formaldehyde, and the gas phase oxidation of various hydrocarbons with or without a catalyst, to form a variety of products.

Thermodynamic and Detailed Physical Data

For thermodynamic properties of the saturated liquid and vapor and for the super heated vapor, see Tables 3 and 4, respectively. For compressibility data, see Table 5.

Thermodynamic Functions of Air As Ideal Gas @ 26.85 °C

Heat Capacity, C_p°	6.956 kJ/(kmol·°K)
	6.956 J/(mol·°K)
	1.662 cal/(mol·°C)
Entropy, S°	47.533 kJ/(kmol·°K)
	47.533 J/(mol·°K)
	11.361 cal/(mol·°C)
Enthalpy Function	2 080.144 J/mol
	497.166 cal/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of air, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] F. Din in *Thermodynamic Functions of Gases*, F. Din, editor, *1962*, Volume 2, p. 39, Butterworth Inc., Washington, D. C.

[3] *Compressed Gas Handbook*, J. S. Kunkle, S. D. Wilson and R. A. Cota, editors, *1969*, p 481, NASA-SP-3045, U. S. Government Printing Office, Washington, D. C.

[4] See reference 2, pp 39–40.

[5] See reference 2, pp 50–52.

[6] See reference 2, pp 53–55.

[7] See reference 2, pp 46–49.

[8] J. Hilsenrath, *et al.*, *Tables of Thermal Properties of Gases, 1955*, pp 29–32, National Bureau of Standards Circular 564, U. S. Government Printing Office, Washington, D. C.

VAPOR PRESSURE—kPa

Table 3. THERMODYNAMIC PROPERTIES OF THE SATURATED LIQUID AND VAPOR (4)

Pressure			Temperature, °K		Entropy J/(mol·°K)		Enthalpy J/mol		Latent Heat of Vaporization J/mol	Specific Volume cm^3/mol		Density kg/m^3	
kPa	Bar	atm	Liquid (Bubble)	Vapor (Dew)	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
101.325	1.013 25	1	78.8	81.8	0.0	74.00	0	5 942	5 942	33.14	6 456.7	873.9	4.485
202.650	2.026	2	85.55	88.31	4.19	70.30	349	6 096	5 747	34.39	3 389.1	842.1	8.545
303.975	3.040	3	90.94	92.63	6.81	68.03	585	6 176	5 591	35.40	2 319.0	818.1	12.488
506.625	5.066	5	96.38	98.71	10.39	64.98	926	6 251	5 325	36.94	1 427.6	784.0	20.286
709.275	7.093	7	101.04	103.16	13.05	62.84	1 196	6 280	5 084	38.21	1 029.1	757.9	28.141
1 013.250	10.132	10	106.47	108.35	16.34	60.42	1 549	6 284	4 735	40.00	718.4	724.0	40.312
1 519.875	15.199	15	113.35	114.91	20.83	57.37	2 063	6 233	4 170	43.21	464.8	670.2	62.306
2 026.500	20.265	20	118.77	120.07	24.67	54.76	2 527	6 120	3 593	46.63	330.4	621.1	87.651
2 533.125	25.331	25	123.30	124.41	28.08	52.25	2 966	5 960	2 994	50.37	246.6	574.9	117.437
3 039.750	30.398	30	127.26	128.12	31.40	49.64	3 412	5 740	2 328	55.69	186.6	520.0	155.198
3 546.375	35.464	35	130.91	131.42	35.40	46.60	3 930	5 399	1 469	64.90	134.2	446.2	215.797
3 766.250	37.662	37.17	132.52 (max) point of contact		41.36		4 755		0	90.52		319.929	
3 774.356	37.744	37.25	132.42 (plait point)		41.00		4 707		0	88.28		328.047	

Table 4. THERMODYNAMIC PROPERTIES OF SUPERHEATED AIR

H, ENTHALPY, kJ/mol (5); **S**, ENTROPY, J/(mol·°K) (6); **V**, SPECIFIC VOLUME, cm^3/mol (7)

Pressure				Temperature, °K												
kPa	bar	atm		100	125	150	200	250	260	280	300	320	360	400	450
101.325	1.013 25	1	H	6.493	7.245	7.993	9.471	10.933	11.224	11.806	12.388	12.971	14.139	15.309	16.775
			S	80.09	86.83	92.28	100.79	107.31	108.45	110.61	112.62	114.50	117.94	121.02	124.47
			V	8 031	10 146	12 233	16 373	20 495	21 319	22 965	24 610	26 255	29 543	32 830	36 937
202.650	2.026	2	H	6.455	7.217	7.971	9.457	10.924	11.216	11.799	12.382	12.966	14.135	15.306	16.773
			S	74.11	80.91	86.41	94.97	101.52	102.67	104.83	106.84	108.72	112.16	115.24	118.69
			V	3 926	5 016	6 078	8 167	10 238	10 651	11 477	12 302	13 126	14 473	16 418	18 474
506.625	5.066	5	H	6.296	7.119	7.901	9.417	10.897	11.191	11.779	12.365	12.951	14.124	15.299	16.769
			S	65.43	72.78	78.48	87.21	93.82	94.97	97.15	99.17	101.06	104.52	107.62	111.08
			V	1 456	1 937	2 385	3 244	4 084	4 251	4 584	4 916	5 248	5 911	6 571	7 396
1 013.250	10.132	10	H		6.922	7.771	9.348	10.853	11.151	11.744	12.335	12.926	14.106	15.286	16.762
			S		65.91	72.11	81.19	87.91	89.08	91.28	93.32	95.23	98.71	101.81	105.28
			V		905.5	1 152.2	1 602.6	2 032.6	2 117.5	2 286.5	2 454.8	2 622.6	2 956.6	3 288.8	3 703.2
2 026.500	20.265	20	H		6.392	7.484	9.204	10.764	11.069	11.675	12.277	12.876	14.070	15.261	16.749
			S		56.98	64.97	74.89	81.85	83.05	85.30	87.38	89.31	92.82	95.96	99.46
			V		374.0	533.5	782.1	1 007.3	1 051.1	1 138.1	1 224.4	1 310.2	1 479.9	1 647.9	1 857.3
4 053.000	40.530	40	H			6.767	8.909	10.584	10.904	11.536	12.159	12.776	13.999	15.211	16.722
			S			55.56	68.02	75.51	76.76	79.11	81.25	83.24	86.84	90.03	93.58
			V			219.8	372.8	496.0	519.3	565.2	610.4	654.8	742.3	828.2	934.7
6 079.500	60.795	60	H			5.566	8.599	10.403	10.739	11.397	12.041	12.676	13.927	15.161	16.694
			S			45.52	63.45	71.53	72.85	75.29	77.51	79.56	83.24	86.49	90.09
			V			98.6	237.5	326.6	343.0	375.2	406.5	437.1	479.0	555.4	627.6
8 106.000	81.060	80	H			4.905	8.285	10.224	10.576	11.260	11.926	12.579	13.856	15.111	16.666
			S			39.97	59.87	68.55	69.93	72.46	74.76	76.87	80.63	83.94	87.60
			V			68.7	171.3	242.7	255.7	280.8	305.0	328.8	374.9	419.4	474.4
10 132.500	101.325	100	H			4.599	7.987	10.051	10.419	11.130	11.818	12.488	13.790	15.065	16.639
			S			37.08	56.88	66.13	67.57	70.20	72.57	74.73	78.57	81.93	85.63
			V			58.9	133.3	193.0	203.8	224.7	244.7	264.2	301.8	338.1	382.7
20 265.000	202.650	200	H			4.123	7.105	9.419	9.835	10.637	11.405	12.144	13.560		
			S			30.51	47.77	58.13	59.76	62.73	65.38	67.76	71.93		
			V			46.4	70.4	100.0	105.7	116.8	127.5	137.9	157.7		
25 331.250	253.312	250	H			4.116	6.926	9.240	9.664	10.485	11.273	12.034	13.491		
			S			28.96	45.20	55.56	57.22	60.27	62.99	65.44	69.73		
			V			44.0	61.3	83.7	88.2	97.0	105.5	113.8	129.8		
30 397.500	303.975	300	H			4.178	6.845	9.135	9.561	10.389	11.189	11.965	13.453		
			S			27.90	43.29	53.54	55.21	58.28	61.04	63.54	67.92		
			V			42.4	55.9	73.5	77.2	84.4	91.4	98.3	111.6		
35 463.750	354.638	350	H				6.832	9.086	9.511	10.341	11.147	11.933			
			S				41.84	51.92	53.59	56.67	59.45	61.99			
			V				52.3	66.7	69.8	75.8	81.7	87.5			
40 530.000	405.300	400	H				6.863	9.079	9.502	10.331	11.140	11.931			
			S				40.70	50.59	52.25	55.32	58.11	60.66			
			V				49.7	61.8	64.4	69.6	74.7	79.7			

Table 5. COMPRESSIBILITY FACTOR FOR AIR, Z = PV/RT (8)

PRESSURE, kPa; atm SHOWN BELOW kPa VALUES IN PARENTHESES

Temperature, °K	101.325 (1)	405.3 (4)	709.3 (7)	1 013.2 (10)	4 053.0 (40)	7 092.8 (70)	10 132.5 (100)
100	0.980 90						
150	0.994 07	0.975 91	0.957 16	0.937 8	0.683 2		
200	0.997 67	0.990 67	0.983 67	0.976 66	0.908 0	0.848 1	0.810 5
250	0.999 06	0.996 24	0.993 52	0.990 82	0.966 80	0.949 8	0.941 7
300	0.999 70	0.998 79	0.997 97	0.997 17	0.991 35	0.990 0	0.993 3
350	1.000 02	1.000 08	1.000 21	1.000 35	1.003 26	1.009 0	1.017 6
400	1.000 19	1.000 79	1.001 41	1.002 05	1.009 46	1.018 8	1.029 9
500	1.000 34	1.001 37	1.002 42	1.003 48	1.014 54	1.026 5	1.039 3
600	1.000 38	1.001 52	1.002 67	1.003 85	1.015 74	1.028 1	1.040 8
700	1.000 38	1.001 53	1.002 68	1.003 85	1.015 58	1.027 5	1.039 7
800	1.000 37	1.001 48	1.002 59	1.003 71	1.014 93	1.026 3	1.037 9
900	1.000 35	1.001 40	1.002 46	1.003 51	1.014 11	1.024 8	1.035 6
1 000	1.000 33	1.001 32	1.002 31	1.003 31	1.013 25	1.023 3	1.033 3
1 500	1.000 24	1.000 98	1.001 71	1.002 45	1.009 78	1.017 1	1.024 4
2 000	1.000 35	1.000 85	1.001 40	1.001 96	1.007 6	1.013 2	1.018 8
2 500	1.003 6	1.002 4	1.002 4	1.002 6	1.006 6	1.011 0	1.015 5
3 000	1.025 2	1.013 3	1.010 7	1.009 5	1.009 2	1.011 9	1.015 1

VAPOR PRESSURE—kPa

ALLENE

(Synonym: Propadiene)
(Formula; CH_2:C:CH_2 or C_3H_4)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.040 065 kg
One Mole of C_3H_4	0.040 065 kg
Specific Volume @ 21.1 °C, 101.325 kPa	599.3 dm^3/kg; 9.6 ft^3/lb
Vapor Pressure @ 21.1 °C	873.5 kPa; 8.74 bar; 116.7 psig; 8.62 atm
Boiling Point @ 101.325 kPa	238.65 °K; −34.5 °C; −30.1 °F
Freezing Point @ 101.325 kPa	136.85 °K; −136.3 °C; −213.3 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	1.415
Density, Liquid @ Saturation Pressure @ −20 °C	0.647 kg/l
Critical Temperature	393.15 °K; 120.0 °C; 248.0 °F
Critical Pressure	5 239 kPa; 52.4 bar 759.8 psia; 51.7 atm
Critical Volume	4.049 dm^3/kg
Critical Density	0.247 kg/dm^3
Critical Compressibility Factor	0.281
Flammability Limits In Air	1.5–11.5% (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	60.84 kJ/(kmol·°K); 60.84 J/(mol·°K); 14.54 cal/(mol·°C) 0.363 Btu/(lb·°F)
Viscosity, Gas @ 101.325 kPa @ 0 °C	0.007 6 mPa·s; 0.007 6 $mN·s/m^2$; 0.007 6 cP
Viscosity, Liquid @ −80 °C	0.380 mPa·s; 0.380 $mN·s/m^2$; 0.380 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.015 69 W/(m·°K); 37.5 x 10^{-6} cal·cm/(s·cm^2·°C
Thermal Conductivity, Liquid @ −40 °C	0.148 43 W/(m·°K); 354.8 x 10^{-6} cal·cm/(s·cm^2 °C)
Surface Tension @ −40 °C	16.5 mN/m; 16.5 dyn/cm
Heat of Combusion, Gas @ 25 °C and Constant Pressure Gross, to form H_2O(liq) + CO_2(gas)	1 944.35 kJ/mol; 464.71 kcal/mol
Net, to form H_2O(gas) + CO_2(gas)	1 856.32 kJ/mol; 443.67 kcal/mol

Description

The simplest member of the 1,2-diene class of compound is allene. Allenes are not as stable as conjugated dienes (1,3-dienes) or isolated dienes. Allene is slightly more strained than the isomeric methylacetylene. It isomerized to methylacetylene in the presence of strongly basic substances, such as sodamide in liquid ammonia or potassium hydroxide in ethanol.

Allene is a colorless, flammable gas at room temperature and atmospheric pressure. it is readily liquefied and is shipped as a liquefied gas under its own vapor pressure of 703 kPa (102 psig) at 21.1 °C.

Specifications

Allene has a minimum purity of 97%.

Uses

Allene is of interest chiefly in organic synthesis.

Toxicity

The toxicity of allene has not been fully investigated. It may have slight narcotic properties and act as a simple asphyxiant. Allene should always be handled with adequate ventilation.

First Aid Suggestions

Exposure to high concentrations of allene may cause intoxication and loss of coordination. Persons with such symptoms should be removed to uncontaminated air and a physician called at once. If the exposure was severe enough to cause unconsciousness, oxygen should be administered. If breathing

has stopped, start artificial respiration immediately and call a physician at once.

Precautions in Handling and Storage

Allene is hazardous because of its extreme flammability. Store and use allene in well-ventilated areas away from heat and all sources of ignition such as flames and sparks. Never use flames to detect leaks of allene; use a soap water solution. Do not use allene around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of allene cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all lines and equipment used with allene.

In addition, the general rules stated in Appendix I should be observed.

Leak Detection

Leaks of allene in lines and equipment may be detected by painting the suspected sites with soapwater solution; leaks will be evident by bubble formation.

Disposal of Leaking Cylinders

Confer Appendix II-A for disposal procedure.

Materials of Construction

Since allene is non-corrosive, most common or commercially available metals may be used. If allene is to be used under pressure at elevated temperatures, isomerization to methylacetylene may occur and in this event copper and silver and their alloys should not be used because of the possibility of forming explosive acetylides. Piping systems and vessels to contain allene should be designed to have a working pressure as specified by competent engineers using a safety factor conforming to the ASME code for pressure piping.

Cylinder and Valve Description

Allene is shipped in DOT approved steel cylinders. Cylinders of allene are equipped with Compressed Gas Association (CGA) valve outlet No. 510, having a thread size of 0.885 inch diameter, left-hand internal threads accepting a bullet-shaped nipple (see Figure 1). Lecture bottles have a special dual valve

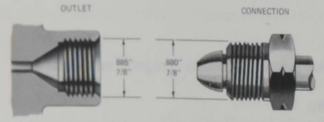


Fig. 1. CONNECTION 510 .885"-14 LH INT. accepting a Bullet Shaped Nipple

$^{9}/_{16}$ inch-R. H. male and $^{5}/_{16}$ inch-32 threads per inch female outlet.

Safety Devices

Cylinders of allene have as safety devices spring-loaded safety relief valves. If the cylinder pressure becomes dangerously high (usually due to overheating) the safety relief device will open at approximately 2 586 kPa (375 psig) and release allene until the pressure again returns to a safe level.

Recommended Controls

Automatic Pressure Regulators

Matheson supplies automatic pressure single stage regulator Model 1P-510 for allene service. The delivery pressure range of this regulator is 28–240 kPA (4–35 psig). The regulator has a brass body and fabric reinforced neoprene rubber diaphragm. No cylinder pressure gauge is necessary in this regulator since it would not indicate cyclinder content, but only vapor pressure which will remain constant as long as liquid remains in the cylinder. Cylinder content is determined by weight. To prevent suckback, a check valve is recommended for use with the regulator. This regulator is not satisfactory for pressures below 14 kPa (2 psig). For this purpose, Matheson supplies a Model 70 low pressure regulator. This regulator has an oversized pancake body of die cast aluminum with a Buna-N diaphram. The Model 70-510 regulator has a delivery pressure range of 3.4–34.5 kPa (0.5–5 psig). It gives sensitive and very accurate low pressure control.

Single stage regulator Model 3321 with delivery pressure range 28–410 kPa (4–60 psig) is recommended for use with lecture bottles.

Manual Controls

Matheson needle valve Model 50-510, a brass bar stock valve, is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets (¼" NPT male or female pipe, or ¼" compression fitting) but is usually supplied with a serrated hose end. The valve is used for intermittent flow control directly from the cylinder, but it requires constant attention by the user. Such a manual flow control will not effectively control pressure and should not be used where pressure control is necessary.

Needle valve Model 31B is recommended for use with lecture bottles.

Flowmeters

Matheson series 7600 laboratory brass flowmeter units of the rotameter type are recommended where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

VAPOR PRESSURE—kPa

Matheson

Shipping Regulations

Allene is classified by the DOT as a flammable, compressed gas and is shipped with the required "Red Gas Label".

Chemical Preparation

Allene is made by the action of zinc dust on 2,3-dichloropropene or 2,3-dibromopropene in 2-methoxyethanol. Pyrolysis of isobutylene at 600–885 °C under controlled pressure and contact time gives a mixture of allene and methylacetylene in yields of about 60 mole %. It is also obtainable by the electrolysis of potassium itaconate.

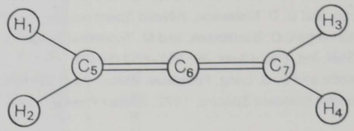
Chemical Reactions

The following reactions are presented to indicate the scope of the reactivity of allene. Allene and the related 1,2-dienes are distinguished from other dienes by their isomerization to acetylenes on treatment with metallic sodium or sodamide. Isomerization of allene to methylacetylene is also effected in the vapor phase with hydrogen fluoride at 300 °C. In the presence of sulfuric acid, allene may be hydrated to acetone, probably through the intermediate formation of the enol form CH_2:$C(OH)CH_3$. Allene reacts with alcoholic potassium hydroxide to give ethyl isopropenyl ether. Allene reactions with hydrogen cyanide to form 2-methylacrylonitrile CH_2:$C(CH_3)CN$ and crotononitrile CH_3CH:$CHCN$. Bromine (2 moles) adds to allene to give 1,2,2,3-tetrabromopropane. Hypochlorous acid reacts with allene in two ways: (a) to give dichloracetone $ClCH_2COCH_3Cl$, and (b) to give 2-chloro-2-propen-1-ol CH_2:$CClCH_2OH$ which can react further to form 1-chloro-3-hydroxy-2-propanone $ClCH_2COCH_2OH$. Allene reacts with diazomethane CH_2N_2 in ether at elevated pressures and temperatures to form methylenepyrazoline. Tetrafluoroethylene adds to allene at 150 °C to give 1,1,2,2-tetrafluoro-3-methylenecyclobutane.

Thermodynamic and Detailed Physical Data

Molecular Structure

Allene is a linear molecule with the two CH_2 groups perpendicular to one another. The molecule has V_2 symmetry (2). The structural parameters of allene as determined by electron diffraction (3) are as follows: C_5═C_6 bond distance 1.311 6 × 10^{-6} m (1.311 6 Å); C_5—H bond distance 1.081 6 × 10^{-10} m (1.081 6 Å); H_1—H_2 distance 1.858 2 × 10^{-10} m (1.858 2 Å); H_1—H_3 distance 3.725 0 × 10^{-10} m (3.725 0 Å); H—C—H bond angle 118.5°. The notation for the allene molecule is shown below.



Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous allene.

Vapor Pressure (4)

Vapor pressure values between −100 and 120 °C are shown below.

Temperature (°C)	kPa	Vapor Pressure bar	atm
−100	1.24	0.012 4	0.012 2
−80	8.31	0.083 1	0.082
−60	31.0	0.310 0	0.306
−40	88.96	0.889 6	0.878
−20	193.5	1.935	1.91
0	386.0	3.860	3.81
20	758.9	7.589	7.49
40	1 206.8	12.068	11.91
60	1 792.4	17.924	17.69
80	2 895.9	28.959	28.58
100	3 861.5	38.615	38.11
120 (CT)	5 239.5	53.395	51.71 (CP)

See Figure 3 for vapor pressure vs temperature curve.

Latent Heat of Vaporization, ΔHv

Temperature (°C)	ΔHv, kJ/kg
−80	135.5
−40	125.0
0	111.0
40	95.0
80	73.5

Thermodynamic Properties of Allene as Ideal Gas @ 25 °C

Heat Capacity, C_p°	58.994 J/(mol·°K)
Entropy, S°	243.927 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_{273}^\circ$	1.431 kJ/mol
Enthalpy of Formation, ΔH_f°	192.13 kJ/mol
Free Energy of Formation ΔF_f°	202.38 kJ/mol

Matheson

VAPOR PRESSURE—kPa

REFERENCES

[1] For extensive tabulations of the physical and thermodynamic properties of allene, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] M. Avram and G. D. Mateescu, *Infrared Spectroscopy, 1972*, p. 193, John Wiley & Sons, Inc., New York, New York.

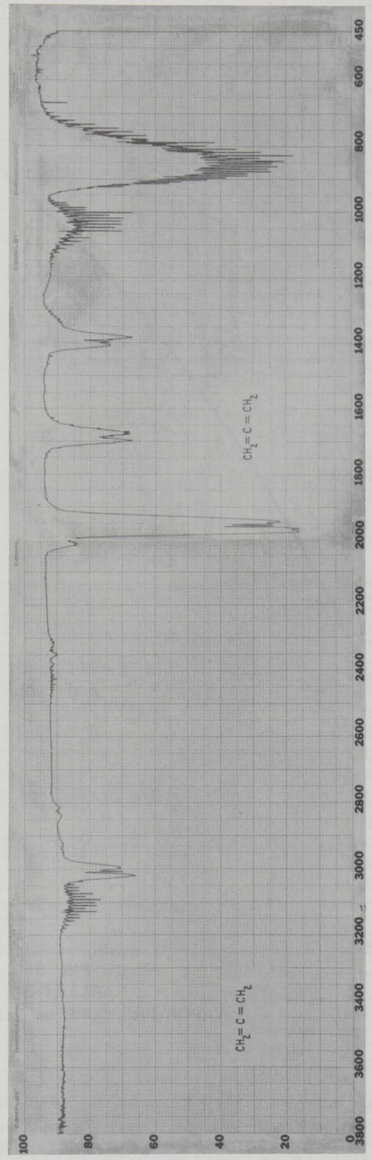
[3] A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand. 13*, 1699 (1959).

[4] D. R. Stull, *Ind. Eng. Chem. 39*, 517–550 (1947).

[5] K. A. Kobe and E. G. Long, *Petroleum Refiner 28*, 133–136 (1949).

[6] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Matheson



Reprinted through the courtesy of Sadtler Research Laboratories

® Sadtler 1972

Fig. 2. High resolution infrared spectrum of gaseous allene in the frequency range 3 800–450 cm^{-1}; 10-cm path length cell, with KBr windows; cell pressure: 6.666 kPa (50 mmHg) (6).

Matheson

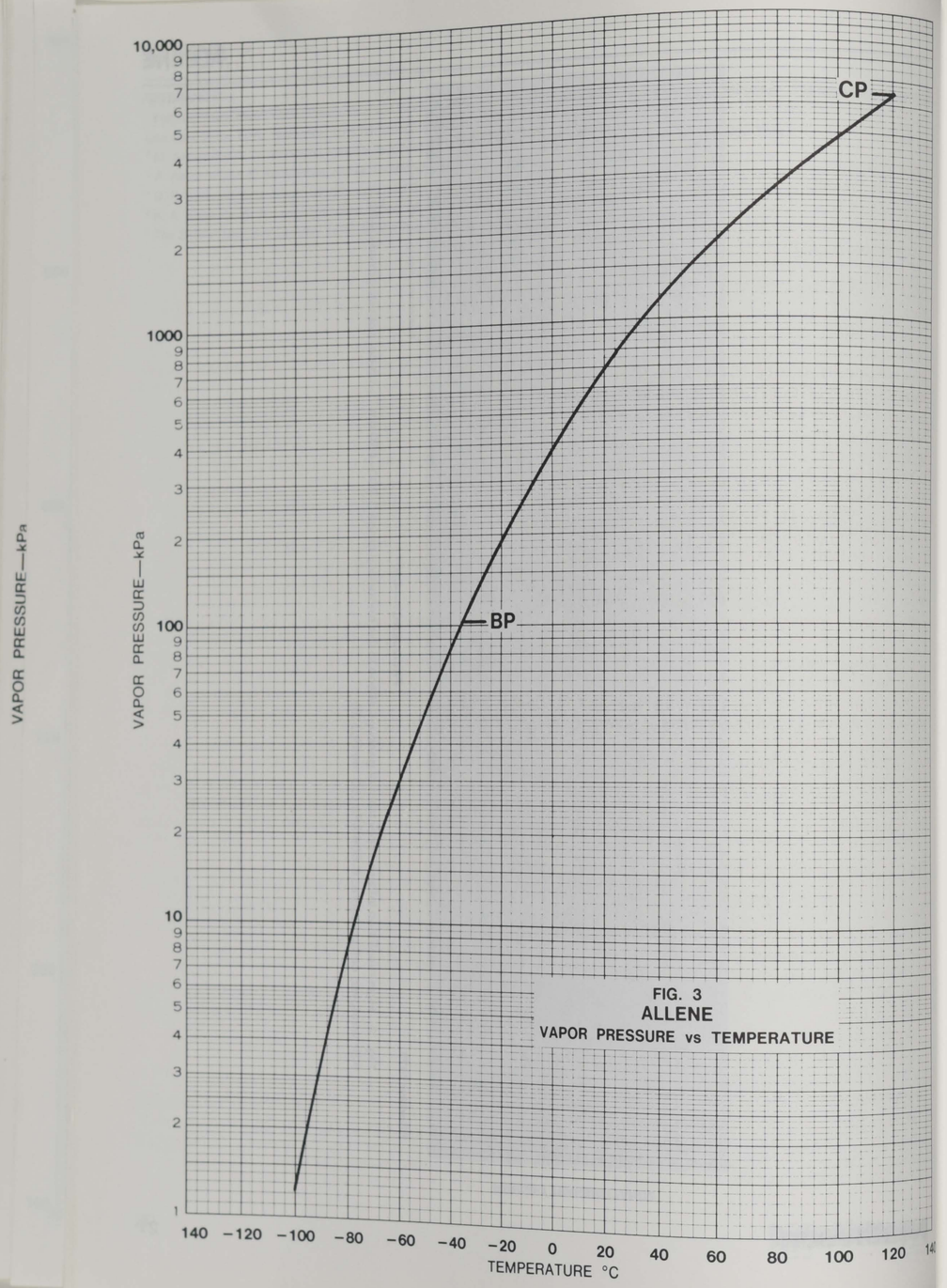


FIG. 3
ALLENE
VAPOR PRESSURE vs TEMPERATURE

AMMONIA

(Synonym: Anhydrous Ammonia)
(Formula: NH_3)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.017 031kg
One Mole of NH_3	0.017 031 kg
Specific Volume @ 21.1 °C, 101.325 kPa	1 410.9 dm^3/kg; 22.6 ft^3/lb
Vapor Pressure @ 21.1 °C	888.0 kPa; 8.88 bar; 128.8 psia; 8.76 atm
Boiling Point @ 101.325 kPa	239.72 °K; −33.4 °C; −28.2 °F
Triple Point	
Temperature	195.41 °K; −77.7 °C; −107.9 °F
Pressure	6.077 kPa; 60.77 mbar; 45.58 mmHg
Absolute Density, Gas @ 101.325 kPa @ 25 °C	0.706 7 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air=1)	0.597
Density, Liquid @ Saturation Pressure @ −33.7 °C	0.682 8 kg/l
Critical Temperature	405.55 °K; 132.4 °C; 270.3 °F
Critical Pressure	11 277 kPa; 112.77 bar; 111.3 atm
Critical Volume	4.251 dm^3/kg
Critical Density	0.235 kg/dm^3
Critical Compressibility Factor	0.242
Latent Heat of Fusion @ −77.7 °C	5.655 kJ/mol; 1 351.6 cal/mol
Flammability Limits In Air	15–28% (by volume)
Dipole Moment, Gas	4.9×10^{-30} C·m; 1.47 D
Molar Specific Heat, Gas @ 101.325 kPa @ 46.8 °C	
@ Constant Pressure	36.953 kJ/(kmol·°K) 36.953 J/(mol·°K) 8.832 cal/(mol.°C)
@ Constant Volume	28.28 kJ/(kmol·°K) 28.28 J/(mol·°K) 6.76 cal/(mol·°C)
Specific Heat Ratio, Gas @ 101.325 kPa @ 46.8 °C, Cp/Cv	1.307
Molar Specific Heat, Saturated Liquid @ −77.7 °C	73.136 kJ/(kmol·°K) 73.136 J/(mol·°K) 17.480 cal/(mol·°C)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.009 82 mPa·s 0.009 82 $mN·s/m^2$ 0.009 82 cP
Viscosity, Liquid @ −33.5 °C	0.255 mPa·s 0.255 $mN·s/m^2$ 0.255 cp
Thermal Conductivity, Gas @ 101.325 kPa @ 0 °C	0.022 18 W/(m·°K) 53.0×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ 10 °C	0.501 7 W/(m·°K) 11.99×10^{-4} cal·cm/(s·cm^2·°C)
Surface Tension @ −40 °C	44.55 mN/m 44.55 dyn/cm
Solubility In Water @ 101.325 kPa (total pressure) @ 20 °C	34.6 kg NH_3/100 kg of solution[3]
Autoignition Temperature	924 °K; 651 °C; 1 204 °F
Refractive Index, Gas @ 101.325 kPa, n_D @ 25 °C	1.000 344 2
Dielectric Constant	
Gas @ 0 °C	1.007 2
Liquid @ −33.4 °C	22.4

Description

At room temperature and atmospheric pressure, ammonia is a colorless, alkaline gas having a pungent order. Ammonia dissolves readily in water. It is shipped as a liquefied gas under its own vapor pressure 787 kPa (114.1 psig) at 21.1 °C.

Specifications

Matheson supplies two grades of ammonia: an Electronic Grade and an Anhydrous Grade. The Electronic Grade has a minimum purity of 99.998% in the liquid phase. The Anhydrous Grade has a minimum purity of 99.99%.

Matheson

VAPOR PRESSURE—vp

Uses

Anhydrous ammonia is one of the oldest commercial refrigerants known. It is used in both absorption and compression type systems. Its most extensive use from the standpoint of volume is in soil fertilization. In this application it is used in the form of ammonia, ammonia salts, nitrates, and urea. It is also used to ammoniate fertilizers containing superphosphates and in making nitrogen solutions which are water solutions of ammonia and ammonium nitrate, or urea, or both. Anhydrous ammonia is applied to the soil by direct injection or by addition to irrigation water.Ammonia, or dissociated ammonia, is used in such metal treating operations as nitriding, carbo-nitriding, bright annealing, furnace brazing, sintering, sodium hydride descaling, atomic hydrogen welding, and other applications where protective atmospheres are required. Dissociated ammonia is also used as a convenient source of hydrogen for the hydrogenation of fats and oils. Through the controlled combustion of dissociated ammonia in air, a source of pure nitrogen is achieved.

The petroleum industry utilizes anhydrous ammonia in neutralizing the acid constituents of crude oil and in protecting equipment such as bubble plate towers, heat exchangers, condensers, and storage tanks from corrosion.

Ammonia is used in extracting such metals as copper, nickel, and molybdenum from their ores.

Ammonia can be oxidized to nitric oxide which is converted to nitrogen dioxide to ultimately furnish nitric acid (Ostwald process); in the lead chamber process for manufacturing sulfuric acid, ammonia is oxidized to nitrogen oxides which are needed to convert sulfur dioxide to sulfuric acid. Most industrial and military explosives of the conventional types contain nitrogen, and ammonia is the basic source of nitrogen in their manufacture.

As a processing agent, ammonia is used in the manufacture of alkalis, ammonium salts, dyes, pharmaceuticals, cuprammonium rayon, and nylon.

A diluted solution of ammonia in water is used as a common household cleansing agent. More concentrated forms are used extensively as chemical reagents.

A recent development is the substitution of ammonia for calcium in the bisulfite pulping of wood. This improves the yield and quality of the pulp. Ammonia is also used as a solvent for casein in the coating of paper.

Ammonia is used in the rubber industry for stabilization of raw latex to prevent coagulation during transportation and storage.

Ammonia is used as a catalyst in the phenol-formaldehyde condensation and also in the urea-formaldehyde condensation to make synthetic resin.

Anhydrous ammonia is used in combination with chlorine to purify municipal and industrial water supplies.

Effects in Man (2) (3)

Ammonia acts principally on the upper respiratory tract, where it exerts an alkaline, caustic action. It produces respiratory reflexes such as coughing and arrest of respiration. It affects the conjunctiva and cornea immediately. Inhalation causes acute inflammation of the respiratory organs, cough, edema of the lungs, chronic bronchial catarrh, secretion of saliva and retention of urine.

Acute Toxicity (4)

Systemic Effects

Ammonia is not a systemic poison.

Local Effects

Inhalation of high concentrations produces violent coughing due to the local action on the respiratory tract. If rapid escape is not possible, severe lung irritation, pulmonary edema and death can result. Lower concentrations cause eye irritation, laryngitis and bronchitis. See Table 1 for effects of various concentrations of gas in air.

Swallowing of the liquid results in severe corrosive action of the mouth, throat, and stomach.

Exposure to high gas concentrations may cause temporary blindness and severe eye damage. Direct contact of the eyes with liquid anhydrous ammonia will produce serious eye burns.

Liquid anhydrous ammonia produces skin burns on contact.

Chronic Toxicity (4)

Chronic irritation to the eyes, nose, and upper respiratory tract may result from repeated exposure to the vapors.

Threshold Limit Value (TLV)

The 1979 ACGIH has adopted a TLV of 25 ppm (18 mg/m^3), with 35 ppm (27 mg/m^3) adopted as a Short Term Exposure Limit (STEL).

First Aid Treatment (3) (4) (5)

The first aid treatment (as suggested in references 3, 4, and 5) should be carried out at once.

General

Speed in removing ammonia from contact with the patient and in moving him to an uncontaminated atmosphere is of primary importance. Summon a physician immediately for anyone who has been burned or overcome by ammonia. Until a physician arrives, and after having accomplished as thorough removal of ammonia as possible, keep the patient warm and quiet, and take such specific action as may be indicated.

Specific Actions

Inhalation

The conscious person who has inhaled a concentration of ammonia which causes irritating effects should go to an uncontaminated area and inhale fresh air or oxygen. Eye, nose, and throat irritation should be treated as described below for more serious exposures. However, if the exposure has been to minor concentrations for a limited time, usually no treatment will be required. A worker overcome by ammonia must be carried to an uncontaminated atmosphere and, if breathing is labored or has ceased, given artifical respiration (back-pressure, armlift, or mouth-to-mouth resuscitation) immediately, preferably by

trained personnel. When breathing has been restored, 100% oxygen is administered, but not for more than 1 hour of continuous treatment at one time. Oxygen therapy may be interrupted after 1 hour and reinstituted as the clinical condition indicates. Observe for laryngeal spasm and perform tracheostomy if indicated. In case of severe exposure, the patient should breathe 100% oxygen under positive exhalation pressure (4 cm) for one-half hour periods every hour. Treatment may be continued in this way until symptoms subside or other clinical indications for interruption appear.

Contact With Skin

If skin contact is extensive and emergency showers available, the victim should get under the emergency shower immediately. Contaminated clothing and shoes should be removed under the shower. In other cases, the affected areas should be washed thoroughly with large amounts of running water for at least 15 minutes. Do not apply salves or ointments to skin burns during the 24 hour period following the injury. Subsequent medical treatment is otherwise the same as for thermal burns.

Contact With Eyes

Call a physician at once. Immediately begin irrigation of the eyes with copious amounts of clean water while holding the eyelids apart. Continue irrigation for 15 minutes. Repeat this procedure every 10 min for an hour, each time irrigating for a period of 5 minutes. If readily available, a 5% boric acid solution may be used instead of water, but irrigation must not be delayed while such a solution is sought or prepared. Prompt and thorough irrigation is of primary importance.

Any standard anesthetic solution for ophthalmic use ordered by the physician may be instilled for control of severe pain, but only after the 15 minute period of irrigation has been completed. Continuous cold boric acid compresses should be used for cases of severe injury, in addition to irrigation. No oils or ointments should be instilled until after the eye has been examined by a qualified physician, and then only as prescribed by him. Ulcers of the cornea should be treated by an ophthalmologist.

Contact With Nose and Throat

Irrigate the nose and mouth continuously for 15 minutes. If the patient can swallow, encourage him to drink large quantities of ½% citric acid solution or lemonade.

Taken Internally

If liquid anhydrous ammonia has been swallowed, call a physician immediately. If the patient is conscious and able, he should drink large amounts of water to dilute the chemical. Do not induce vomiting if the patient is in shock, extreme pain or is unconscious. If vomiting begins, place the patient face down with head lower than hips; this prevents vomitus from entering the lungs and causing further injury.

Precautions in Handling and Storage

The following specific precautions in addition to the general precautions given in Appendix I should be observed:

1. Anyone working with ammonia should wear rubber gloves, chemical goggles, and a rubber or plastic apron.
2. Ammonia cylinders should never be directly heated by steam or flames. Uncontrolled heating of a cylinder can cause the liquid to expand to a point where dangerous hydrostatic pressures will be developed. Any heating should be done in a thermostated water or oil bath. The temperature should not be allowed to exceed 51.7 °C (125 °F). Cylinders containing less than 165 pounds of ammonia are not equipped with safety devices.
3. Withdrawal of gas should be performed in a well-ventilated area or in a hood.
4. A gas mask approved by the Bureau of Mines and a water supply (showers and eye-bath) should be conveniently located in cases of emergency.
5. Weigh ammonia cylinders to determine contents. The tare weight is stamped on all cylinders.

6 Manifolded cylinders of ammonia should have check valves at the cylinder outlets to prevent exchange of material from one cylinder to another and causing a cylinder to become overfull.

7. Although ammonia does not represent a serious flammability hazard, mixtures of air and ammonia containing from 15 to 28% ammonia by volume will ignite when sparked or exposed to temperatures exceeding 648.9 °C (1 200 °F); therefore, flames and sparks should not be allowed in the area where ammonia is being used.
8. Since ammonia is extremely soluble in aqueous solutions, a trap or check valve should be used to prevent the suckback of materials into the cylinder. Suckback can cause an extremely corrosive condition to form within a cylinder, aside from the possibility of having a violent reaction take place within the cylinder. Any accidental suckback should be reported to the supplier immediately.

Leak Detection and Control

Leaks can be detected by passing an open bottle or a squeeze bottle containing concentrated hydrochloric acid in the vicinity of the suspected leak. Dense white fumes of ammonium chloride will be formed at the leak site. Wet red litmus or phenolphthalein paper will undergo a color change in an ammonia atmosphere and are of aid in detecting small ammonia leaks.

Serious leaks that cannot be stopped in a reasonable amount of time should be doused with water which will take up the ammonia and prevent the atmosphere from becoming contaminated.

Cylinder valves may develop leaks through the packing which can be stopped by tightening up on the packing nut. The packing nut is tightened by turning counter-clockwise as viewed from above since the threads are left hand.

Leaks through the valve outlet that cannot be stopped by shutting off the valve can be stopped by inserting ⅜" pipe plugs in the valve outlet.

Disposal of Leaking Cylinders

Consult Appendix II-B for procedure of disposal of leaking ammonia cylinders.

VAPOR PRESSURE—kPa

Analytical Detection

The concentration of ammonia in air can be determined with the Matheson Kitagawa Toxic Gas Detector Model 8014K, which gives accurate, dependable, and reproducible results. Detector tubes Model 105SA are used for high concentrations (1–25%) and Model 105SC for low (5–260 ppm) concentration ranges of ammonia. A color stain is produced in the detector tube which varies in length with the concentration of the sample being measured. The concentration is then read directly from the tube.

The concentration of ammonia in air can also be determined by titration. A known volume of the air is passed through two bubblers in series containing a known volume of standardized 0.02 N sulfuric acid, the solution in each bubbler combined quantitatively, and the excess acid titrated with standardized 0.02 N sodium hydroxide, using methyl red indicator.

A colorimetric method using Nessler reagent is also available to determine small amounts of ammonia (6).

Materials of Construction

Iron and steel are recommended for all equipment coming in contact with ammonia. Copper, tin, zinc and their alloys are attacked by moist ammonia and should not be used. Piping should be rigid steel except where short connections are needed such as between cylinders and manifold or pipe lines. For these applications a steel reinforced, flexible, neoprene line is recommended.

For permanent installations, tongue and groove, flanged fittings with lead or asbestos composition gaskets are recommended. In order to reduce maintenance all joints should be welded wherever possible.

Wherever there is a possibility of trapping liquid ammonia in lines that become shut off at both ends, the line should be protected by a properly vented relief valve.

Ammonia can combine with mercury to form explosive compounds. Any instruments containing mercury that will be exposed to ammonia should not be used.

Cylinder and Valve Description

Cylinder valves are made of forged steel, and are of the packed type. The outlet for anhydrous ammonia is designated as Compressed Gas Association (CGA) connection No. 240. The thread specifications are ⅜"-18 NGT-RH-INT, being comparable to a ⅜" female pipe size. This outlet is designated as standard by the CGA. (See Figure 1 for the drawing and specifications on this valve outlet and mating connection), Lecture bottles have a special $^{5}/_{16}$"-32 threads per inch female, valve outlet.

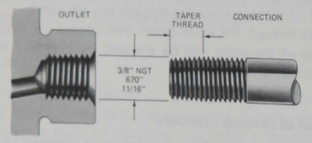


Fig. 1. CONNECTION 240 ⅜"-NGT RH INT. IPS accepting. Tapered.

Cylinders of ammonia containing 15 pounds or more are usually equipped with goose neck dip tubes. Withdrawal of vapor is accomplished with the cylinder standing in the vertical position. On occasion, a full cylinder standing in the sun will heat up and cause the liquid to expand and cover the end of the dip-tube. In this instance it is necessary to allow the cylinder to cool before the vapor can be withdrawn or the cylinder must be placed horizontally with the valve outlet facing down.

In order to withdraw liquid ammonia the cylinder should be placed horizontally with the valve outlet facing up.

The outlet for Electronic Grade ammonia is designated as cylinder valve outlet CGA No. 660. (See Figure 2 for the drawing and specifications on this valve outlet and mating connection).

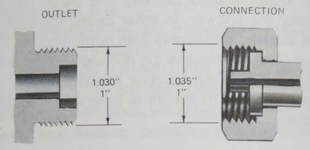


Fig. 2. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders containing less than 165 pounds of ammonia are not required to be equipped with safety devices.

Recommended Controls

Automatic Pressure Regulators

Matheson supplies the single stage regulator Model 12-240 for Anhydrous Grade ammonia service to regulate the vapor phase. This regulator is constructed of an anodized aluminum body with type 316 stainless steel internal parts. The diaphram is constructed of FEP Teflon on a Viton rubber base and the regulator seat is made of Kel-F. The regulator has a delivery pressure range of 28–550 kPa 4–80 psig.

Single stage regulator Model 3501-660 is recommended for use with Electronic Grade ammonia. All metal parts of this regulator in the gas stream are of type 316 stainless steel. It also contains a stainless steel diaphragm packless outlet valve. The helium leakage rate can be certified not to exceed 2×10^{-10} cm^3 per second inboard. The delivery pressure range is 0–170 kPa (0–25 psig).

The Model No. 71-240 regulator is recommended for sensitive and very accurate low pressure control of Anhydrous Grade ammonia. The regulator has an oversized, pancake body of aluminum, with type 303 stainless steel internal parts, with a Teflon-faced Butyl rubber diaphragm and a Teflon seat. The delivery pressure range is 3.4-34.5 kPa (0.5-5 psig).

The Model No. 71S-660 regulator is recommended for sensitive and very accurate low pressure control of Electronic Grade ammonia. The regulator has an oversized pancake body of aluminum, with type 303 stainless steel internal parts, with a 302 stainless steel diaphragm and a Teflon seat. The delivery pressure range is 3.4-41 kPa (0.5–6.0 psig).

Manual Controls

A bar stock steel needle valve Model 61-240 can be supplied where noncritical manual flow control of the liquid or vapor phase is required. This valve is equipped with an outlet having either a serrated hose end, ¼" compression fitting, or ¼" NPT male or female connection. Stainless steel needle valves Model 32S or Model 59 are available for use with the lecture bottles.

A stainless steel check valve Matheson Model 401N should be used to prevent suckback of foreign materials into regulators, gas lines, and cylinders.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Ammonia is shipped under Department of Transportation (DOT) regulations as a nonflammable, compressed gas, taking a DOT "Green Label". It must be shipped in steel containers having a service pressure of not less than 3 310 kPa (480 psig). Cylinders containing less than 165 pounds of ammonia do not require safety devices.

Commercial Preparations

Ammonia is produced primarily by the Haber process whereby nitrogen and hydrogen are combined directly. A less important method is the calcium cyanamide process which produces ammonia from limestone, carbon, nitrogen, and steam. Also some ammonia is obtained from destructive distillation of coal.

Chemical Properties

1. Ammonia is a highly associated, stable compound. Temperatures of 840–930 °C cause slight dissociation at atmospheric pressure.
2. Ammonia with protonic acids gives ammonium salts which (with a few exceptions) are readily soluble in water and uniformly unstable to heat.
3. Ammonia and air heated to 600 °C and passed over a platinum catalyst constitutes the Oswald process for the manufacture of nitric acid.
4. The hydrogen atoms of ammonia may be successively replaced by metal atoms to form amides, imides, and nitrides, and by organic radicals to give primary, secondary, and tertiary amines.
5. Ammonia is a highly reactive chemical. Extensive references to its reactions are available in the technical and patent literature. Esters, acid anhydrides, acyl halides, carbon dioxide, and sulfonyl chlorides form amides when treated with ammonia. Amines are formed when ammonia is reacted with halogen compounds, polyhydric phenols, alcohols, and epoxy compounds.
6. Ammonia does not support ordinary combustion, but it does burn with a yellowish flame in an atmosphere of air or oxygen. The ignition temperature of ammonia-air mixtures is 780 °C. The products of combustion are mainly nitrogen and water, but small traces of ammonium nitrate and nitrogen dioxide are also found.

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

Under certain conditions, mixtures of ammonia and air will explode when ignited. The explosive range for dry ammonia-air mixtures is about 16–25% ammonia. The explosive range is broadened by (1) admixture with other combustible gases such as hydrogen, (2) admixture of oxygen replacing air, and (3) temperatures and pressures higher than atmospheric.

7. Gaseous ammonia is oxidized to water and nitrogen by many oxides—for example, copper oxide. If a stream of ammonia gas is passed over heated copper oxide, the following reaction takes place:

$$3CuO + 2NH_3 + \rightarrow 3Cu + N_2 + 3H_2O$$

This type of reaction occurs when ammonia is heated to a relatively high temperature with oxides of the less positive metals, that is, those to which the oxygen is less firmly bound. Oxidizing agents, if sufficiently powerful, will bring about a similar reaction at ordinary temperatures. With potassium permanganate the following reaction occurs:

$$2NH_3 + 2KMnO_4 \rightarrow 2KOH + 2MnO_2 + 2H_2O + N_2$$

The action of chlorine on ammonia can also be regarded as an oxidation reaction.

$$8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$$

Ammonia can be oxidized to nitric oxide by passing a mixture of air and 10% ammonia through a catalyst at elevated temperature as shown by the equation:

$$4NH_3 + 5O_2 \rightarrow NO + 6H_2O$$

8. Chlorine, bromine, and iodine all react with ammonia. The initial stages of the reactions are similar, although the final products are quite different. The action of chlorine or bromine upon ammonia solution, where the ammonia is in excess, results in the liberation of nitrogen and the formation of the corresponding salt, either chloride or bromide. It is quite probable that substitution first takes place and that the resulting trihalide combines loosely with another molecule of ammonia—

for example, $NCl_3 \cdot NH_3$. These trichloro and tribromo compounds are very unstable and decompose in the presence of excess ammonia to form the ammonium chloride or bromide and free nitrogen.

$$NCl_3 \cdot NH_3 + 3NH_3 \rightarrow N_2 + 3NH_4Cl$$

The iodine compound is more stable and separates as so-called "nitrogen iodine", $NI_3 \cdot NH_3$, an insoluble brownish-black solid. When exposed to light in the presence of ammonia, it decomposes in the same way as the chlorine or bromine derivatives.

$$NI_3 \cdot NH_3 \rightarrow N_2 + 3HI$$

$$NI_3 \cdot NH_3 + 3HI \rightleftarrows 2NH_3 + 3I_2$$

With the ammonia salts, however, the action is different. Chlorine replaces hydrogen and yellow droplets separate. This material which is oily in nature and capable of spontaneous explosive decomposition, is nitrogen chloride.

$$NH_4Cl + 3Cl_2 \rightarrow NCl_3 + 4HCl$$

9. Ammonia reacts with phosphorus vapor at red heat to give nitrogen and phosphine.

$$2NH_3 + 2P \rightarrow 2PH_3 + N_2$$

10. Sulfur vapor and ammonia react to give ammonium sulfide and nitrogen.

$$8NH_3 + 3S \rightarrow 3(NH_4)_2S + N_2$$

Sulfur also reacts with liquid anhydrous ammonia to produce nitrogen sulfide.

$$10S + 4NH_3 \rightarrow 6H_2S + N_4S_4$$

When brought in contact with carbon at red heat, ammonia reacts to form ammonium cyanide.

11. Ammonia forms a great variety of "addition compounds" or coordination compounds. Compounds regarded as addition compounds are often called ammoniates, in analogy with hydrates. Thus, $CaCl_2 \cdot 6NH_3$ and $CuSO_4 \cdot 4NH_3$ are comparable to $CaCl_2 \cdot 6H_2O$ and $CuSO_4 \cdot 4H_2O$, respectively. Such compounds, when regarded as coordination compounds, are often called ammines and are written as complexes—for example, $[Cu(NH_3)_4]SO_4$.

Thermodynamic and Detailed Physical Data

Molecular Structure

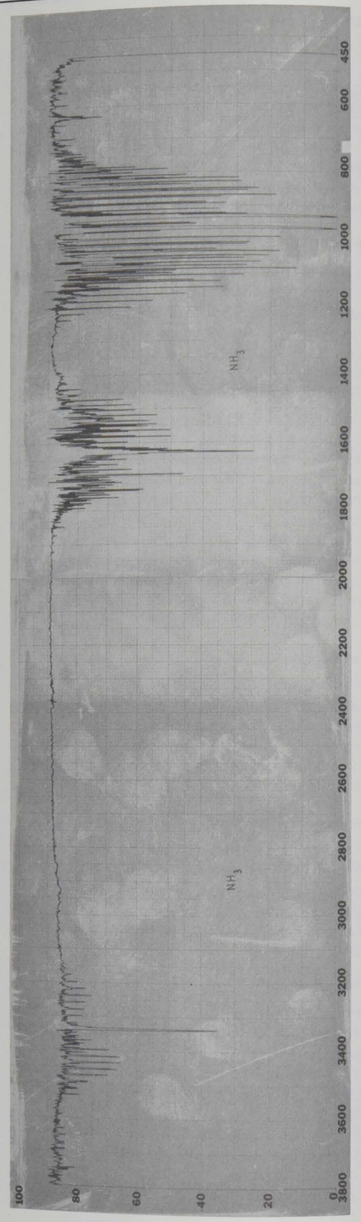
The ammonia molecule is a symmetric pyramidal structure having C_3 symmetry, with a symmetry number of 3. The N—H bond distance is $1.012\,4 \times 10^{-10}$ m (1.0124 Å) and the H—N—H bond angle is 106.67°.

Infrared Spectrum

See Figure 3 for the infrared spectrum of gaseous ammonia.

Vapor Pressure

For vapor pressure data on liquid ammonia, see Table 1 and Figure 4.



Reprinted through the courtesy of Sadtler Research Laboratories
©Sadtler 1972

Fig. 3. High resolution infrared spectrum of gaseous ammonia in the frequency range 3 800–450 cm^{-1}, 10-cm path length cell, with KBr windows; pressure: 2.666 kPa (20 mmHg) (8).

Latent Heat of Vaporization

See Table 1 for data.

Thermodynamic Data

Thermodynamic properties of saturated ammonia are shown in Table 2, while those for superheated ammonia are shown in Table 3.

Thermodynamic Properties of Ammonia As Ideal Gas @ 25 °C (7)

Heat Capacity, C°	35.627 J/(mol·°K)
Entropy, S°	192.602 J/(mol·°K)
Free Energy Function, ($F^\circ_{298} - H^\circ_{298}/T$)	−192.602 J/(mol·°K)
Enthalpy Difference, $H^\circ_{298} - H^\circ_0$	10.058 kJ/mol
Enthalpy of Formation, ΔH°_f	−45.898 kJ/mol
Free Energy of Formation, ΔF°_f	−16.380 kJ/mol

REFERENCES

[1] For an extensive tabulation of the thermodynamic and physical properties of ammonia, see W. Braker and A. L. Mossman, *Matheson Unabridged Gas Data Book, 1974*, Matheson, East Rutherford, New Jersey.

[2] M. B. Jacobs, *The Analytical Toxicology of Industrial Inorganic Poisons, 1967*, p. 610, John Wiley & Sons, Inc., New York, New York.

[3] M. H. Gleason, *et al, Clinical Toxicology of Commercial Products, 1969*, pp. III-16-III-20, The Williams and Wilkens Company, Baltimore, Maryland.

[4] *Anhydrous Ammonia*, Safety Data Sheet SD-8, *1960*, Manufacturing Chemists' Association, Washington, D. C.

[5] W. B. Deichmann and H. W. Gerarde, *Toxicology of Drugs and Chemicals, 1969*, p. 95, Academic Press, Inc., New York, New York.

[6] See reference 2, pp. 612–613.

[7] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Ser., National Bureau of Standards, NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[8] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[9] P. Davies in *Thermodynamic Functions of Gases*, F. Din, editor, *1962*, Volume 1, p. 89, Butterworth, Inc., Washington, D. C.

[10] **Ibid.**, pp. 90–91.

[11] **Ibid.**, pp. 92–93.

[12] **Ibid.**, pp. 94–95.

Vapor Concentration (ppm)	General Effects	Exposure Period
50–53	Odor detectable by most persons	Prolonged repeated exposure produces no injury
100	No adverse effects for average worker	Maximum allowable concentration for 8-hour working day
300	Maximum concentration tolerated without serious disturbances	1 hour
400–700	Nose and throat irritation. Eye irritation with tearing	Infrequent short (1 hour) exposures ordinarily produces no serious affect
2 000–3 000	Convulsive coughing	No permissible exposure
5 000–10 000	Severe eye irritation Respiratory spasm Rapid asphyxia	May be fatal after short exposure No permissible exposure Rapidly fatal

Table 1.

Table 2. THERMODYNAMIC PROPERTIES OF THE SATURATED LIQUID AND VAPOR (9)

Temperature		Pressure			Entropy J/(mol•°K)		Enthalpy kJ/mol		Latent Heat of Vaporization kJ/mol	Specific Volume cm^3/mol		Density kg/dm^3	
°K	°F	kPA	bar	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
195.42	−107.9	6.076 5	0.060 8	0.059 97	71.59	199.95	10.435	35.522	25.087				
200	−99.7	8.666 3	0.086 7	0.085 53	73.30	198.41	10.770	35.794	25.024	23.37	189 730	0.729	0.000 09
210	−81.7	17.792 7	0.177 9	0.175 6	76.90	194.26	11.510	36.158	24.648	23.74	96 858	0.717	0.000 18
220	−63.7	33.913 5	0.339 1	0.334 7	80.33	190.54	12.255	36.497	24.242	24.13	53 070	0.706	0.000 32
230	−45.7	60.612 6	0.606 1	0.598 2	83.63	187.11	13.008	36.794	23.786	24.55	30 895	0.694	0.000 55
240	−27.7	102.581	1.025 8	1.012 4	86.86	183.89	13.770	37.054	23.284	24.99	18 905	0.682	0.000 90
250	−9.7	165.362	1.654	1.632 0	90.00	181.13	14.535	37.317	22.782	25.46	12 088	0.669	0.001 41
260	8.3	255.947	2.559	2.526	93.01	178.57	15.309	37.560	22.251	25.96	8 029	0.656	0.002 12
270	26.3	381.894	3.819	3.769	95.94	176.23	16.096	37.773	21.677	26.50	5 505	0.643	0.003 09
280	44.3	551.816	5.518	5.446	98.78	174.05	16.887	37.961	21.074	27.07	3 882	0.629	0.004 39
290	62.3	775.339	7.753	7.652	101.59	172.00	17.694	38.120	20.426	27.70	2 803	0.615	0.006 08
300	80.3	1 062.393	10.62	10.485	104.31	170.08	18.506	38.238	19.732	28.39	2 066	0.600	0.008 24
310	98.3	1 424.933	14.25	14.063	106.98	168.24	19.330	38.317	18.987	29.14	1 545	0.584	0.011 02
320	116.3	1 873.50	18.74	18.49	109.62	166.40	20.171	38.388	18.217	29.98	1 174	0.568	0.014 51
330	134.3	2 421.67	24.22	23.90	112.21	164.77	21.033	38.380	17.347	30.92	900.1	0.551	0.018 92
340	152.3	3 082.31	30.82	30.42	114.77	163.01	21.924	38.305	16.381	31.99	696.1	0.532	0.024 47
350	170.3	3 869.60	38.70	38.19	117.32	161.00	22.840	38.137	15.297	33.24	540.4	0.512	0.031 52
360	188.3	4 802.81	48.03	47.40	119.87	158.99	23.799	37.878	14.079	34.73	419.3	0.490	0.040 62
370	206.3	5 891.04	58.91	58.14	122.47	156.73	24.807	37.472	12.665	36.58	323.9	0.466	0.052 58
380	224.3	7 153.55	71.54	70.60	125.27	153.97	25.832	36.807	10.975	39.03	247.0	0.436	0.068 95
390	242.3	8 606.55	86.06	84.94	128.28	150.58	27.087	35.736	8.649	42.61	182.6	0.400	0.093 27
400	260.3	10 284.5	102.8	101.5	130.00	145.10	28.514	33.731	5.217	49.45	124.5	0.344	0.136 80
405.6	270.4	11 297.7	113.0	111.5	138.24		31.066		0.0	72.47		0.235	

Table 3. THERMODYNAMIC PROPERTIES OF SUPERHEATED VAPOR

H, ENTHALPY, J/mol (10); **S**, ENTROPY, J/(mol·°K) (11); **V**, SPECIFIC VOLUME, cm^3/mol (12)

Pressure kPa	atm		Temperature, °K 300	320	340	360	380	400	420	440	460	480	500	520	540	560	580
101.325	1	H	39 304.5	40 015.8	40 756.3	41 517.6	42 296.1	43 078.5	43 865.1	44 655.8	45 459.2	46 279.2	47 111.8	47 961.2	48 823.1	49 693.4	50 576.2
		S	192.422	194.723	196.941	199.075	201.125	203.091	205.016	206.857	208.656	210.413	212.129	213.802	215.434	217.024	218.572
		V	24 384	26 069	27 743	29 410	31 072	32 730	34 386	36 040	37 692	39 342	40 991	42 639	44 287	45 934	47 581
506.625	5	H	38 923.8	39 702.0	40 492.8	41 291.9	42 095.2	42 902.7	43 710.2	44 517.8	45 337.8	46 170.4	47 019.8	47 877.5	48 747.8	49 626.4	50 513.4
		S	178.197	180.707	183.092	185.351	187.527	189.619	191.627	193.552	195.393	197.150	198.865	200.539	202.213	203.803	205.351
		V	4 659	5 037	5 399	5 753	6 102	6 447	6 790	7 130	7 468	7 805	8 141	8 476	8 810	9 143	9 475
1 013.3	10	H	38 358.9	39 245.9	40 120.4	40 994.8	41 840.0	42 685.2	43 517.8	44 350.4	45 191.4	46 040.7	46 902.6	47 772.9	48 651.6	49 542.7	50 438.1
		S	170.707	173.552	176.230	178.740	181.125	183.385	185.519	187.527	189.410	191.167	192.882	194.556	196.230	197.861	199.451
		V	2 181	2 402	2 606	2 799	2 985	3 166	3 344	3 520	3 694	3 867	4 039	4 210	4 380	4 549	4 717
2 533.1	25	H			38 865.2	40 020.0	41 053.4	42 015.7	42 923.7	43 823.2	44 722.8	45 626.5	46 534.4	47 446.6	48 362.9	49 283.3	50 212.2
		S			165.770	168.950	171.837	174.473	176.858	179.033	181.042	182.924	184.724	186.481	188.196	189.912	191.544
		V			908.2	1 014	1 106	1 192	1 274	1 353	1 429	1 503	1 576	1 648	1 720	1 791	1 862
5 066.3	50	H					39 346.3	40 651.7	41 802.3	42 865.1	43 890.2	44 902.7	45 902.7	46 890.1	47 873.3	48 852.4	49 827.3
		S					162.548	166.021	168.992	171.544	173.803	175.895	177.862	179.786	181.669	183.468	185.226
		V					463.8	526.5	579.3	627.5	672.7	715.6	756.8	796.8	835.8	873.9	911.1
10 132.5	100	H						34 819.2	38 919.6	40 601.5	42 032.5	43 337.9	44 547.0	45 718.6	46 852.4	47 948.6	49 019.7
		S						147.821	157.695	161.670	164.850	167.695	170.163	172.464	174.556	176.565	178.489
		V						138.2	221.1	258.4	291.0	319.9	346.1	370.4	393.4	415.5	436.9
16 212	160	H							30.932.3	36 208.3	39 074.4	41 124.5	42 714.5	44 116.1	45 380.0	46 560.0	
		S							136.984	149.369	155.854	160.247	163.594	166.272	168.657	170.875	
		V							55.4	103.7	141.5	167.5	188.8	207.8	225.5	242.3	
20 265	200	H							29 685.5	33 082.9	36 802.5	39 430.0	41 350.5	42 936.2	44 308.6	45 547.0	
		S							133.177	141.336	149.494	155.687	159.662	162.674	165.310	167.611	
		V							45.4	61.7	89.9	115.6	137.1	154.6	170.4	185.2	
26 345	260	H							29 024.4	31 388.4	34 241.9	37 011.7	39 371.4	41 283.5	42 852.5	44 233.2	
		S							131.001	136.524	142.925	149.411	154.306	158.030	161.000	163.511	
		V							41.2	48.3	59.9	75.9	92.5	107.6	121.5	134.1	
30 398	300	H							28 798.5	30 898.8	33 350.7	35 919.6	38 279.4	40 300.3	41 986.4	43 438.3	
		S							130.081	135.060	140.708	146.356	151.377	155.352	158.574	161.251	
		V							39.6	44.5	52.6	63.7	76.3	88.8	101.1	112.6	
36 477	360	H							28 585.1	30 509.7	32 618.5	34 827.6	37 032.6	39 070.2	40 844.2	42 358.8	
		S							129.160	133.762	138.670	143.553	148.114	152.005	155.436	158.323	
		V							38.0	41.6	46.8	53.8	62.4	71.7	81.2	90.6	
40 530	400	H							28 484.7	30 346.6	32 308.8	34 367.4	36 446.8	38 425.9	40 191.5	41 722.8	
		S							128.658	133.093	137.654	142.214	146.524	150.331	153.762	156.607	
		V							37.1	40.4	44.5	49.9	56.6	64.3	72.4	80.5	
50 663	500	H							28 321.5	30 078.5	31 890.4	33 718.9	35 547.3	37 321.3	38 978.1	40 522.0	
		S							127.445	131.670	135.687	139.704	143.469	147.026	150.289	153.051	
		V							35.3	37.8	40.6	44.5	48.5	53.3	58.6	64.4	
60 795	600	H							28 258.7	29 957.4	31 677.1	33 375.8	35 036.8	36 647.7	38 204.1	39 710.3	
		S							126.399	130.457	134.348	138.030	141.503	144.766	147.821	150.498	
		V							34.2	36.1	38.4	41.2	44.2	47.6	51.5	55.7	

Matheson

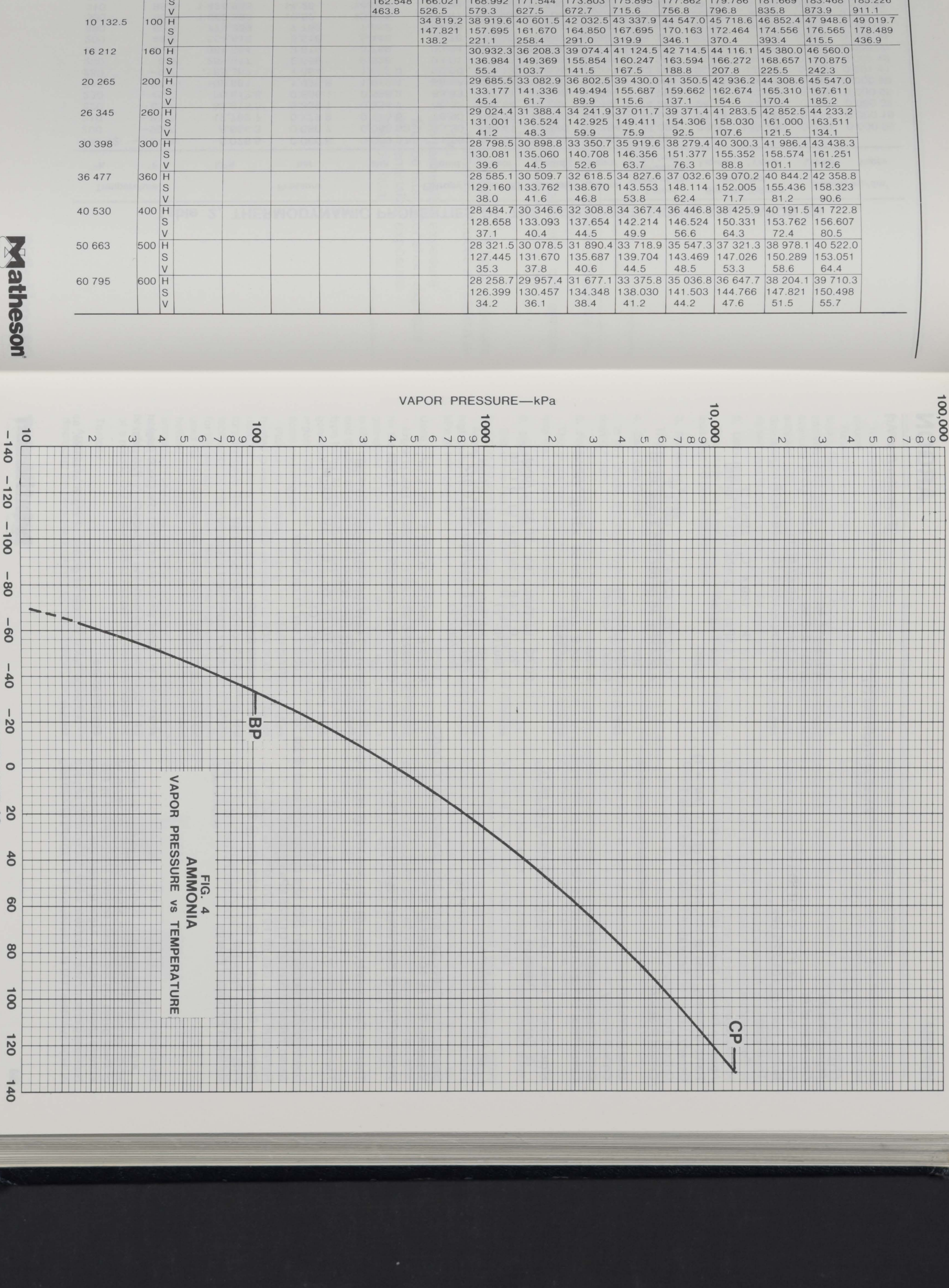


FIG. 4
AMMONIA
PRESSURE vs TEMPERATURE

ARGON

(Formula: A or Ar)

Physical Properties (1)

Atomic Mass	0.039 948 kg
Atomic Weight	0.039 948 kg
One Mole of Ar	603.7 dm^3/kg 9.67 ft^3/lb
Specific Volume @ 21.1 °C 101.325 kPa	87.29 °K; −185.9 °C; −302.6 °F
Boiling Point @ 101.325 kPa	
Triple Point	83.78 °K; −189.4 °C; −308.9 °F
Temperature	68.75 kPa; 687.5 mbar; 515.7 mmHg
Pressure	1.784 1 kg/m^3
Absolute Density, Gas @ 101.325 kPa @ 0 °C	1.380
Relative Density, Gas @ 101.325 kPa @ 0 °C (Air = 1)	
Density, Liquid @ Saturation Pressure See Table 1	
Critical Temperature	150.72 °K; −122.4 °C; −188.4 °F
Critical Pressure	4 864 kPa; 48.64 bar; 705.4 psia. 48.00 atm
Critical Volume	1.884 1 dm^3/kg
Critical Density	0.530 7 kg/dm^3
Critical Compressibility Factor	0.292
Latent Heat of Fusion @ −189.4 °C	1 184.9 J/mol; 29.66 kJ/kg; 283.0 cal/mol
Molar Specific Heat, Gas @ 101.325 kPa @ 26.85 °C	
@ Constant Pressure	20.83 kJ/(kmol·°K); 20.83 J/(mol·°K); 0.124 6 kcal/(kg·°C) 0.1246 Btu/(lb·°F)
@ Constant Volume	12.48 kJ/(kmol·°K); 12.48 J/(mol·°K); 0.074 7 kcal/(kg·°C) 0.074 7 Btu/(lb·°F)
Specific Heat Ratio, Gas @ 101.325 kPa @ 26.85 °C Cp/Cv	1.669
Viscosity, Gas @ 101.325 @ 25 °C	0.022 5 mPa·s; 0.022 5 mN·s/m^2; 0.022 5 cP
Viscosity, liquid @ Saturation Pressure @ −189.2 °C	0.283 mPa·s; 0.283 mN·s/m^2; 0.283 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 26.85 °C	0.017 744 W/(m·°K); 0.425×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −139.2 °C	0.067 W/(m·°K); 1.6×10^{-6} cal·cm/(s·cm^2·°C)
Solubility in Water @ 101.325 kPa (partial pressure) @ 20 °C	0.033 7 cm^3/1 cm^3 water
Sonic Velocity, Gas @ 101.325 kPa @ 0 °C	307.8 m/s
Refractive Index, Gas @ 101.325 kPa, n_D @ 25 °C	1.000 259
Dielectric Constant, Gas @ 101.325 kPa @ 20 °C	1.000 516 59
First Ionization Potential	2.525×10^{-18} J; 15.759 eV
Minimum Excitation Energy	1.850×10^{-18} J; 11.548 eV

VAPOR PRESSURE, LB.

Description

Argon is the most abundant member of the rare gas family which consists of helium, neon, argon, krypton, and xenon. All of these gases are monatomic and are characterized by their extreme chemical inactivity. Argon is a colorless, odorless, and tasteless gas somewhat soluble in water. It is normally shipped in large cylinders (1A) at a pressure of 17 170 kPa (2 490 psig at 21.1 °C, in smaller amounts at 13 790 kPa (2000 psig) at 21.1 °C, and in lecture bottles at 12 240 kPa (1 775 psig) at 21.1 °C.

Specifications

Matheson has a number of grades of argon available, as follows:

Matheson

1. Research Purity

This grade of argon has a minimum purity of 99.9995% by volume.

Research Grade argon is available in small cylinders and liter flasks. Research Grade argon in cylinders is supplied with an analysis of the gas. An Assayed Research Grade argon is also available in liter flasks and small cylinders, the flasks being supplied with an actual analysis of gas. Assayed Research Grade argon in cylinders is supplied with an analysis of the gas as sampled from the specific cylinder contents.

2. Ultra High Purity Grade

This grade has a minimum purity of 99.999% and contains less than 10 ppm total impurities.

3. Matheson Purity

This grade has a minimum purity of 99.9995%.

4. Zero Gas Grade

In this grade, the total hydrocarbons (as methane) is less than 0.5 ppm.

5. Prepurified Grade

This grade has a minimum purity of 99.998% and contains less than 20 ppm total impurities.

6. High Purity Grade

This grade has a minimum purity of 99.995% and contains less than 50 ppm total impurities.

Argon of 99.998% minimum purity is available at special high pressures, namely, 24 130 kPa (3 500 psig) and 41 370 kPa (6 000 psig) at 21.1 °C.

Uses

Argon is used extensively in the incandescent lamp industry for the filling of light bulbs. It is used in arc welding as an inert gas shield to prevent oxidation of the metals being welded. It is also used with other rare gases in the filling of special bulbs and display tubes to obtain special color effects in the neon-type bulbs. Many Geiger-counting tubes contain argon or argon-mixed with organic vapors and gases, particularly 90% argon–10% methane, which is used universally as a proportional counting gas.

Plasma jet torches, utilizing an argon-hydrogen mixture heated to temperatures in excess of 10 000 °K (9 727 °C) are used for cutting operations and for coating metals with refractory materials. The high temperature preparation, refining, and fabrication of many materials must be carried out in an argon (or helium) atmosphere. Most of the high-purity single crystals used for semiconducting devices are grown in an argon (or helium) atmosphere. In doping semiconductors with controlled amounts of impurities, the latter are frequently introduced in a stream of argon (or helium). Argon (or helium) is used extensively to carry a reactant to a reaction zone, to modify the rate of a reaction by dilution and to remove reaction products.

Toxicity

Argon is nontoxic but can act as a simple asphyxiant by displacing the necessary amount of air to support life.

Precautions in Handling and Storage

Do not place cylinders where they may become part of an electric circuit. When electric arc welding, precautions must be taken to prevent striking an arc against a cylinder.

In addition, the general rules stated in Appendix I should be observed.

Leak Detection

Leaks of argon in lines and equipment setups may be detected by painting the suspected sites with soap water; leaks will be evident by bubble formation. Matheson Leak Detectors Model 8016 and Model 8017 provide a more sensitive method of leak detection.

Disposal of Leaking Cylinders

See Appendix II-C for procedure for disposal.

Materials of Construction

Since argon is inert, no special materials of construction are required. However, any piping or vessels containing argon should be adequately designed to have a working pressure as specified by competent engineers, using a safety factor conforming to the ASME code for pressure piping.

Cylinder and Valve Description

Argon is packaged in Department of Transportation (DOT) approved, high pressure steel cylinders.

Matheson employs Compressed Gas Association (CGA) valve outlet connection No. 580 on all cylinders of argon except those at 6 000 psig. This standard cylinder valve outlet has a diameter of 0.965 inch and right-hand internal threads, accepting a bullet-shaped nipple (see Figure 1 for this valve outlet and its mating connection). Cylinders at 41 370 kPa (6 000 psig) are equipped with CGA valve outlet connection No. 677. Lecture bottles have special dual valve $^9/_{16}$″-18 threads per inch male and $^5/_{16}$″-32 threads per inch female valve outlets.

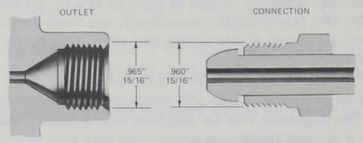


Fig. 1. CONNECTION 580 .965″-14 RH INT. accepting a Bullet Shaped Nipple

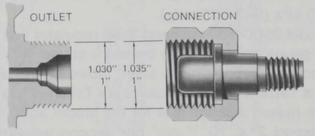


Fig. 2. CONNECTION 677 1.030″-14 LH EXT. accepting Round Shaped Nipple

Matheson

Safety Devices

Cylinders containing argon have safety devices of either the frangible disc type or frangible disc backed up with fusible metal, melting at approximately 100 °C (212 °F). Cylinders pressurized 10% in excess of their marked service pressure in accordance with present DOT regulations must contain only safety devices of the frangible disc type. These safety devices are usually an integral part of the cylinder valve, situated opposite the valve outlet.

Recommended Controls

Automatic Pressure Regulators

In order to reduce the high cylinder pressure of argon to a working value consistent with a system's design the following types of controls are recommended:

1. Single Stage Automatic Regulators

Single Stage Automatic Regulators will reduce cylinder pressure in one stage to a delivery pressure, in a particular range, depending upon the design of the regulator and its spring load. A single stage regulator will show a slight variation in delivery pressure as cylinder pressure falls. The following single stage regulators are available from Matheson for use with the Prepurified and High Purity Grades of argon:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
1L-580	28–550	0.28–5.5	4–80
1H-580	69–1 240	0.69–12.4	10–180
2-580	34.5–4 480	3.45–44.8	50–650
3-580	690–10 340	6.9–103.4	100–1500
4-580	690–17 240	6.9–172.4	100–2500
3320 (for lecture bottles)	28–410	0.28–4.1	4–60

Single stage regulators Model 19-580 and Model 3500-580 with delivery pressure ranges of 28–345 kPa (4–50 psig) and 28–520 kPa (4–75 psig), respectively, are recommended for use with Research Purity Grade and Ultra High Purity Grade argon.

The Model 19 regulator is of all brass construction with a diaphram of German silver with nylon seat and aluminum gaskets. The regulator can be supplied with a helium leak rate check if desired (maximum acceptable leak rate is 2×10^{-9} cm^3 per second). It is provided with a packless outlet valve (Model 4373P) with a ¼" Gyrolok tube fitting. It has two 2½" gauges, a delivery pressure gauge of 0–690 kPa (0–100 psig) or 0–1 380 kPa (0–200 psig) and a cylinder pressure gauge of 0–20 680 kPa (0–3 000 psig).

The Model 3500-580 stainless steel regulator has a cylinder pressure gauge and a delivery pressure gauge. All parts in the gas stream are 316 stainless steel, including the diaphragm. The seat is Tefzel® and the gaskets are Teflon; it has no rubber parts. The helium leakage rate for the Model 3500 is certified not to exceed 2×10^{-10} cm^3 per second inboard. It has a delivery pressure range of 28–520 kPa (4–75 psig).

Low pressure regulator Model 70 is recommended for use with Prepurified Grade and High Purity Grade argon. It is designed for use with the Model 1L-580 regulator; inlet pressure to the Model 70 regulator must not exceed 1 720 kPa (250 psig). The delivery pressure range is 3.4–34.5 kPa (0.5–5 psig).

2. Two Stage Regulators

This type of regulator performs the same function as single stage regulators. However, greater accuracy and control of the delivery pressure is maintained, and the delivery pressure does not vary as cylinder pressure falls. The following two stage regulators are available from Matheson:

Model No.	Delivery Pressure Range		
	kPa	Bar (g)	psig
8L-580	14–104	0.14–1.04	2–15
8-580	28–340	0.28–3.4	4–50
8H-580	69–690	0.69–6.9	10–100
9-580	138–1720	1.38–17.2	20–250

The above regulators are recommended for use with Prepurified Grade and High Purity Grade argon. For all other grades of argon, the following two stage regulators are recommended:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
3800-580	28-620	0.28–6.2	4–90
3104-580	28-690	0.28–6.9	4–100

3. Controls For Argon at Special High Pressure

Prepurified argon is also available at 24–150 kPa (3 500 psig) and 41 370 kPa (6 000 psig) in addition to its normal availability at 17 170 kPa (2 490 psig). For 24 130 kPa (3 500 psig) cylinders, metal diaphragm regulators Models 3-580 or 4-580, having delivery pressure ranges of 690–10 340 kPa (100–1 500 psig) and 690–17 240 kPa (100–2 500 psig), respectively, are recommended for use. The regulators are provided with outlet valves having ¼" NPT male connections. Stainless steel fitting adapters, to permit simple connection to ¼" O.D. metal tubing, are also available.

A Model No. 3064 with a brass body Kel-F® seat, 303 stainless steel valve stem, and Viton® "O" rings, with a delivery pressure range of 1 380–24 820 kPa (200–3 600 psig) and a Model No. 3075-580 with a bronze body, neoprene diaphragm, Nylatron seat, 303 stainless steel valve stem and neoprene "O" rings, with a delivery pressure range of 1 380–41 370 kPa (200–6 000 psig) are also available.

For 41 370 kPa (6 000 psig) service the following single stage regulators are available:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
3064-677	172.5–27 600	1.72–276	25–4 000
3066-677	345–41 400	3.45–41.4	50–6 000
3075-677	1 380–41 370	13.8–413.7	200–6 000

Conventional equipment should never be used at these high pressures.

4. Low-Pressure Regulators

The above regulators are not satisfactory for accurate delivery pressures below 34.5 kPa (5 psig). Therefore, an auxilary regulator specifically designed for low pressure is recommended for use in series with any of the above standard type regulators having delivery pressures to 345 kPa (50 psig). Matheson has various models known as the Model 70 regulators which may be obtained with delivery pressures ranging from 0.5 kPa to 69 kPa (10 psig) as follows:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
70B	0.5–3.0	0.005–0.030	2–12 inches water column
70	3.4–34.5	0.034–0.345	0.5–5 psig
70A	34.5–69	0.345–0.69	5–10 psig

For argon, the Model 70 regulator may be used in series with the Model 1L-580 regulator; inlet pressure must not exceed 1 724 kPa (250 psig) to obtain a delivery pressure of 3.4–34.5 kPa (0.5–5 psig).

Manual Controls

Manual needle valves for direct attachment to the cylinder valve outlet are available. These types of controls are mainly used where intermittent flows are necessary, or where it is desired to control the flow of gas directly from the cylinder. This type of a needle valve will allow control of extremely slow flow rates on up to relatively large flow rates. However, pressure cannot be controlled with such a valve, and, if a line or system becomes plugged, dangerous pressures can build up. The following type valves are recommended for use with argon: Model 50-580, Model 52-580 with a gauge to indicate tank pressure. These valves are normally supplied with serrated hose ends, ¼" compression fittings, or ¼" NPT male or female outlets. The Model 30AR and Model 31B control valves are recommended for use with lecture bottles.

Manual valve Model 4351-580 is recommended for use with Research Purity Grade and Ultra High Purity Grade argon.

Flowmeters

Matheson Series No. 7600 laboratory brass flowmeter units with 150 mm flowmeter tubes and floats and Series No. 7200 laboratory brass flowmeter units with 65 mm flowmeter tubes and a single float are recommended for use with argon where accurate flows of a definite value must be known or reproduced.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Argon is shipped in high pressure steel cylinders as a nonflammable, compressed gas, taking a DOT "Green Label". They are usually filled to the marked service pressure of the cylinder or to a maximum of 10% in excess of the marked service pressure in accordance with present DOT regulations.

Commercial Preparations

Argon is recovered from plants producing oxygen and nitrogen. These plants liquefy air which undergoes a distillation process to remove oxygen, nitrogen, argon, and some of the other rare gases.

Chemical Properties

Argon is a monatomic, chemically inactive gas. It will not react with other elements or compounds. While a few compounds of argon and other rare gases are reported to have been prepared, such researches, and the results obtained, may be considered of scientific interest only. For all practical purposes every attempt to make argon combine to give compounds of the usual types, like treatment with oxidizing or reducing agents, has failed. The comparative stability of argon is due to the complete pairing of all electrons present and the absence of any bonding orbitals.

Thermodynamic and Detailed Physical Data

Vapor Pressure

The vapor pressure of liquid argon between −191.525 °C and −178.880 °C is represented by the following Antoine vapor pressure equation (2):

$$\log_{10} p = A - \frac{B}{t + C} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A B and C have the values of 6.616 51, 304.277, and 267.320, respectively.

Some calculated vapor pressure values are shown below:

Temperature, °C	Vapor Pressure		
	kPa	mbar	mmHg
−191.885	53.33	533.3	400
−189.650	66.66	666.6	500
−188.047	79.99	799.9	600
−186.640	93.33	933.3	700
−185.869	101.325	1 013.25	760
−185.380	106.66	1 066.6	800
−184.236	119.99	1 199.9	900
−183.184	133.32	1 333.2	1 000
−181.301	159.99	1 599.9	1 200
−178.880	199.98	1 999.8	1 500

For other vapor pressure data, see Table 1.

Latent Heat of Vaporization

See Table 1.

Thermodynamic Data

The thermodynamic properties of saturated argon are shown in Table 1.

Thermodynamic properties of argon as real gas are shown in Tables 2 and 3.

Thermodynamic Properties of Argon as Ideal Monatomic Gas @ 25 °C (3)

Heat Capacity, C_p^0	20.778 J/(mol·°K); 4.966 cal/(mol·°C)
Entropy, S^0	154.74 J/(mol·°K); 36.98 cal/(mol·°C)
Free Energy Function, $(F^0_{298} - H^0_0)/T$	−133.95 J/(mol·°K); −32.01 cal/(mol·°C)
Enthalpy Difference $H^0_{298} - H^0_0$	6.198 kJ/mol; 1.481 kcal/mol

REFERENCES

[1] For extensive tabulations of thermodynamic and physical properties of argon, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1974*, Matheson, East Rutherford, New Jersey.

[2] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds, 1968*, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[3] G. C. Maitland and E. B. Smith, *J. Chem Eng. Data 17*, 293,297 (1972).

[4] F. Din, *Thermodynamic Functions of Gases, 1962*, Volume 2, p. 181, Butterworth, Inc., Washington, D. C.

[5] See reference 4, pp. 186–189.

[6] See reference 4, pp. 182–185.

[7] See reference 4, pp. 190–193.

[8] *Chemical Engineers' Handbook*, 4th edition, R. H. Perry, C. H. Hilton, and S. D. Kirkpatrick, editors, *1963*, p. 3–102, McGraw-Hill Book Company, New York, New York.

Table 1. THERMODYNAMIC PROPERTIES OF THE SATURATED LIQUID AND VAPOR (4)

Pressure kPa	Pressure bar	Pressure atm	Temp., °K	Entropy J/(mol. °K) Liquid	Entropy J/(mol. °K) Vapor	Enthalpy kJ/mol Liquid	Enthalpy kJ/mol Vapor	Specific Volume cm³/mol Liquid	Specific Volume cm³/mol Vapor	Density kg/dm³ Liquid	Density kg/dm³ Vapor
68.749	0.687	0.6785 (T.P.)	83.78	52.20	131.10	2.826	9.436	28.2	9 961	1.416 6	0.004 01
101.325	1.013 25	1	87.29	53.91	128.57	2.972	9.489	28.7	6 999	1.391 9	0.005 71
202.650	2.026	2	94.43	57.42	124.21	3.293	9.600	29.6	3 714	1.349 7	0.010 76
303.975	3.040	3	99.20	59.73	121.61	3.514	9.652	30.2	2 553	1.322 9	0.015 65
506.625	5.066	5	105.97	63.02	118.32	3.855	9.715	31.3	1 578	1.276 3	0.025 32
709.275	7.093	7	110.98	65.45	116.01	4.128	9.739	32.3	1 144	1.236 8	0.034 92
1 013.250	10.132	10	116.81	68.26	113.51	4.441	9.727	33.4	802.5	1.196 1	0.049 78
1 519.875	15.199	15	124.22	71.63	110.40	4.865	9.684	35.3	529.3	1.131 7	0.075 52
2 026.500	20.265	20	130.03	74.40	107.85	5.241	9.590	37.2	383.6	1.073 8	0.104 14
2 533.125	25.331	25	134.86	76.79	104.59	5.582	9.466	39.6	294.7	1.008 8	0.135 56
3 039.750	30.398	30	139.06	78.95	103.55	5.905	9.326	42.3	233.8	0.944 4	0.170 86
4 053.000	40.530	40	146.12	82.77	99.93	6.499	9.006	48.7	155.6	0.820 3	0.256 67
4 863.600	48.636	48.00 (CP)	150.72	91.41		7.829		75.2		0.531 2	

Table 2. THERMODYNAMIC PROPERTIES OF REAL GAS ARGON

H, ENTHALPY (5), kJ/mol; **S**, ENTROPY (6), J/(mol·°K); **V**, SPECIFIC VOLUME (7), cm³/mol

Pressure kPa	Pressure bar	Pressure atm		Temperature, °K 100	150	200	250	300	350	400	450	500
101.325	1.013 25	1	H	9.759	10.816	11.866	12.910	13.952	14.994	16.034	17.075	18.116
			S	131.48	140.05	146.10	150.76	154.56	157.76	160.55	163.00	165.19
			V	8 056	12 222	16 364	20 485	24 559	28 711	32 819	36 925	41 031
1 013.25	10.132	10	H		10.563	11.729	12.822	13.886	14.943	15.996	17.048	18.099
			S		119.75	126.49	131.37	136.61	138.53	141.31	143.80	146.01
			V		1 140	1 593	2 024	2 447	2 864	3 281	3 696	4 110
2 533.1	25.331	25	H		10.037	11.488	12.675	13.777	14.861	15.935	17.005	18.073
			S		109.58	117.99	123.19	128.73	130.66	133.52	136.04	138.28
			V		392	608	794	971	1 143	1 313	1 481	1 648
5066.2	50.662	50	H			11.050	12.422	13.958	14.732	15.843	16.942	18.037
			S			110.63	116.80	122.56	124.62	127.56	130.15	132.46
			V			280	384.7	479.6	570.4	656.9	743.0	828.4
10 132	101.32	100	H			10.072	11.915	13.247	14.482	15.666	16.828	17.975
			S			101.17	109.50	115.99	118.22	121.34	124.07	126.49
			V			115	182.1	235.4	284.3	329.8	375.0	419.1
20 265	202.65	200	H			8.770	11.009	12.656	14.081	15.404	16.665	17.890
			S			90.85	100.89	108.81	111.37	114.85	117.83	120.43
			V			57.5	88.0	117.4	144.1	168.8	192.3	214.9
30 398	303.98	300	H			8.385	10.529	12.310	13.837	15.236	16.554	17.823
			S			86.36	95.96	104.50	107.23	110.91	114.02	116.70
			V			46.2	63.0	82.1	99.9	116.8	132.4	147.3
50 662	506.62	500	H			8.165	10.196	12.068	13.707	15.173	16.522	17.808
			S			81.15	90.21	99.26	10.218	106.04	109.22	111.93
			V			38.0	47.1	57.7	67.6	77.2	86.1	94.8
101 325	1 013.2	1 000	H			8.576	10.506	12.437	14.150	15.629	16.976	18.258
			S			74.75	83.35	92.72	95.76	99.64	102.81	105.51
			V			32.0	35.9	41.3	45.9	50.3	54.7	58.9
151 987	1 519.9	1 500	H				11.404	13.295	14.964	16.407	17.711	18.946
			S				79.88	89.04	92.01	95.78	98.85	101.45
			V				32.7	35.5	38.7	41.6	44.5	47.3
202 650	2 026.5	2 000	H			10.554	12.377	14.219	15.842	17.235	18.476	19.635
			S			69.24	77.36	86.29	89.18	92.82	95.74	98.18
			V			28.5	30.7	32.7	34.4	35.8	37.2	38.4
303 975	3 039.8	3 000	H			12.722	14.469	16.217				
			S			66.08	73.88	82.33				
			V			26.5	28.2	29.8				
405 300	4 053.0	4 000	H			14.961	16.557	18.359				
			S			63.87	71.45	79.69				
			V			25.3	26.5	28.0				
506 625	5 066.2	5 000	H			17.255	18.914	20.591				
			S			62.42	69.83	77.94				
			V			24.5	25.6	26.8				

VAPOR PRESSURE—kPa

Table 3. COMPRESSIBILITY DATA FOR ARGON (8)
PRESSURE, kPa; atm VALUES SHOWN IN PARENTHESES

Temperature, °K	101.325 (1)	405.3 (4)	709.3 (7)	1 013.25 (10)	4 050.0 (40)	7 093.0 (70)	10 132.5 (100)
100	0.978 2	0.907 9					
150	0.993 0	0.971 6	0.950	0.927			
200	0.997 1	0.988 2	0.979 2	0.970 2	0.897 8	0.783 8	0.691 7
250	0.998 6	0.994 5	0.990 5	0.986 4	0.947 6	0.914 1	0.887 8
270	0.999 0	0.996 0	0.993 0	0.990 0	0.962 2	0.938 8	0.920 8
280	0.999 1	0.996 6	0.994 0	0.991 5	0.967 9	0.948 6	0.934 0
290	0.999 3	0.997 1	0.994 9	0.992 7	0.972 9	0.957 0	0.945 4
300	0.999 4	0.997 5	0.995 7	0.993 8	0.977 3	0.964 3	0.955 3
310	0.999 5	0.997 9	0.996 3	0.994 8	0.981 0	0.970 6	0.963 7
320	0.999 6	0.998 2	0.996 9	0.995 6	0.984 3	0.976 1	0.971 0
350	0.999 8	0.999 0	0.998 3	0.997 7	0.992 1	0.988 8	0.987 9
400	1.000 0	0.999 9	0.999 9	0.999 8	1.000 2	1.002 2	1.005 7
450	1.000 1	1.000 4	1.000 7	1.001 1	1.005 0	1.010 1	1.016 2
500	1.000 2	1.000 7	1.001 3	1.001 8	1.007 9	1.014 7	1.022 4
550	1.000 2	1.000 9	1.001 6	1.002 3	1.009 5	1.017 4	1.025 9
600	1.000 3	1.001 0	1.001 8	1.002 6	1.010 5	1.019 0	1.027 9
650	1.000 3	1.001 1	1.001 9	1.002 7	1.011 1	1.019 8	1.028 9
700	1.000 3	1.001 1	1.001 9	1.002 8	1.011 3	1.020 1	1.029 2
750	1.000 3	1.001 1	1.002 0	1.002 8	1.011 4	1.020 2	1.029 2
800	1.000 3	1.001 1	1.002 0	1.002 8	1.011 3	1.019 9	1.028 8
900	1.000 3	1.001 1	1.001 9	1.002 7	1.011 0	1.019 4	1.027 9
1 000	1.000 3	1.001 0	1.001 8	1.002 6	1.010 5	1.018 5	1.026 5
1 100	1.000 3	1.001 0	1.001 7	1.002 5	1.010 0	1.017 6	1.025 2

ARSINE

(Formula: AsH_3)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.077 946 kg
One Mole of AsH_3	0.077 946 kg
Specific Volume @ 21.1 °C, 101.325 kPa	312.1 dm^3/kg; 5.0 ft^3/lb
Vapor Pressure @ 21.1 °C	1 514.7 kPa; 15.15 bar; 219.7 psig; 14.95 atm
Boiling Point @ 101.325 kPa	210.67 °K; −62.5 °C; −80.5 °F
Triple Point	156.22 °K; −116.9 °C; −178.5 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	3.243 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	2.69
Density, Liquid @ −73.2 °C	1.653 kg/l
Critical Temperature	373.05 °K; 99.9 °C; 211.8 °F
Latent Heat of Fusion @ −116.9 °C	1 195 J/mol; 3.665 kcal/kg
Dipole Moment, Gas	667×10^{-33} C·m; 0.2 D
Viscosity, Gas @ 101.325 kPa @ 0 °C	0.014 58 mPa·s; 0.014 58 mN·s/m^2; 0.014 58 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 0 °C	0.008 912 W/(m·°K); 21.3×10^{-6} cal·cm/(s·cm^2·°C)
Solubility in Water @ 101.325 kPa (partial pressure) @ 20 °C	0.23 cm^3/1 cm^3 water

Description

Arsine is a toxic, colorless gas with a garlic-like odor at room temperature and atmospheric pressure. It is shipped as a liquefied compressed gas under its own vapor pressure of 1 410 kPa (205 psig).

Specification

On a hydrogen-free basis, Electronic Grade arsine has a minimum purity of 99.995%.

Uses

Arsine is used in doping gas mixtures for the preparation of semiconductor materials containing a controlled amount of significant impurity. This is effected by thermal decomposition in a gaseous stream directed onto the surface of a seed of semiconductor material, usually silicon.

Effects in Man and Toxicity (2)

Arsine is a strong hemolytic agent. Exposure causes the following symptoms, generally after some delay (sometimes a day or so): malaise, severe headache, giddiness, nausea, vomiting, diarrhea, pain in the kidneys and liver, jaundice, aliguria, hemoglobinuria, anuria, anemia. In more severe cases the vomiting may be more pronounced, the mucous membranes may have a bluish discoloration and the urine is dark or bloodstained. After a day or two there is severe anemia and jaundice.

In prolonged exposure to low concentrations of arsine, the symptoms have more relation to effects produced by dusts and fumes of arsenic compounds, and albumin may appear along with hemoglobin in the urine. Prolonged exposure of animals to low concentrations of arsine produced a compensated destruction of red blood cells, which gradually deteriorated to a stationary level of anemia. There was little injury to other organs. However, repeated exposure to very low concentrations may have cumulative effects resulting in severe poisoning. A concentration of 500 ppm is lethal for a man after exposure of a few minutes. A concentration of 250 ppm (equivalent to 0.75 mg/l) is dangerous to life in an exposure of 30 minutes. Concentrations of 6.25–15.5 ppm (0.02–0.05 mg/l) are dangerous after exposure for 30–60 minutes. The maximum concentration tolerated for several hours without serious symptoms is 3.1 ppm.

The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 0.05 ppm for arsine (concentration in air to which nearly all personnel may be continuously exposed without adverse affects).

First Aid Suggestions

Summon a physician at once for anyone who has been exposed to arsine. Prior to the physician's arrival first aid measures should be taken. Those presented herein are based upon what is believed to be common practice in industry. Their adoption in any specific case should be subject to the prior endorsement by a competent medical advisor.

Remove victim promptly to an uncontaminated atmosphere. Keep the victim warm (not hot) and quiet. Administer pure

oxygen. If breathing is weak or has stopped, give artificial respiration with simultaneous administration of oxygen.

Suggestions for Medical Treatment (3)

Modern treatment of arsine poisoning includes immediate exchange transfusions, BAL, mannitol diuresis, and urinary alkalinization and dialysis if renal failure supervenes.

The exchange transfusion is carried out with heparinized femoral catheters and may require 10–15 exchanges of whole blood. The plasma hemoglobin concentration is used as guidelines. Attempts should be made to lower the concentration by 75–85% of the plasma hemoglobin and also return the hematocrit level to normal.

Preservation of renal function is essential. Early intravenous mannitol (25–50 g) is given if the patient is oliguric, and bicarbonate is used to alkalinize the urine. If this method fails to reverse the oliguria, the institution of peritoneal or preferably hemodialysis should be undertaken.

There is no specific antidote for arsine poisoning. Dimercaprol (BAL) is given in doses of 2.5 mg/kg. This dosage should be repeated 4 to 6 times the first 2 days and reduced to twice daily for up to 10 days. BAL is given so that it may bind with circulatory oxidation products of arsine after the red cells lyse and prevent acute and chronic toxicity to other organ systems.

Precautions in Handling and Storage

Gas mixtures containing arsine are hazardous because of the high toxicity of the arsine. In addition, if the carrier gas is hydrogen then flammability hazards will also exist. Gas mixtures containing arsine should be used in a well-ventilated area, preferably in a hood with forced ventilation. Personnel handling and using gas mixtures containing arsine should have available for immediate use oxygen generating gas masks of a type approved by the U. S. Bureau of Mines, or self-contained air-breathing apparatus. Additional gas masks should be located in convenient areas near where the arsine is being used in case of emergency. Do not store reserve stocks of arsine gas mixtures with cylinders containing oxygen or other highly oxidizing or flammable materials. Ground all lines and equipment used with arsine.

In addition, the general rules stated in Appendix I should be observed.

Leak Detection

Systems designed to contain arsine should be pretested for leaks with an inert gas such as helium or nitrogen.

Analytical Detection

Arsine in air can be determined by use of mercuric chloride test paper (4), by the diethylidithiocarbamate method (5), or by the molybdenum blue method (6). The first method is the official British method for detecting arsine in air (7).

The atmosphere is drawn by an appropriate hand pump first through lead acetate paper to absorb any traces of hydrogen sulfide before coming in contact with the mercuric chloride test paper (prepared by immersing strips of filter paper in 5% mercuric chloride solution, drying them, and cutting off and discarding the ends). The resulting stain is compared within 5 minutes with the standard stains issued with the leaflet. The concentration of arsine is then found by reference to the color chart, which shows the intensities of stains corresponding with 10–50 strokes of the pump.

Matheson-Kitagawa Toxic Gas Detector Model 8014K is also available for determining the concentration of arsine in the atmosphere. Using Model 140 detector tubes, concentrations in the range of 5–160 ppm are determinable.

In addition, the Matheson Arsine/Phosphine Monitor Model 8040 provides an excellent means of detection of arsine in air at the TLV (50 ppb). The Model 8040 Monitor utilizes a chemically treated tape located between a light source and a photo cell. Ambient air is continuously drawn across the tape, changing the photo cell output. When the tape darkens to a preset level, the built-in alarm sounds continuously until the monitor is reset.

Disposal of Leaking Cylinders

Leaks in cylinders containing arsine gas mixtures which cannot be stopped by tightening up on the cylinder packing nut or by plugging or capping the cylinder valve outlet should be handled in the following manner. If the cylinder is not already stationed in a hood, it should be transferred to one immediately (after first putting on self-contained breathing equipment). Connect an appropriate regulator with flexible tubing to the cylinder valve outlet. Open the cylinder valve and then adjust the regulator valve so that a moderate stream of arsine or the mixture containing arsine is introduced into an adequate quantity of bromine water or sodium hypobromite solution. The arsine will be trapped and oxidized by these solutions. Tag the cylinder as defective, and notify the supplier.

Materials of Construction

Piping and accessories leading to equipment for the thermal decomposition of arsine may be of iron or steel construction and should be adequately designed to withstand pressures to be encountered.

Cylinder and Valve Description

Arsine is shipped in Department of Transportation (DOT) approved, steel cylinders equippped with Compressed Gas Association (CGA) valve outlet connection No. 660, the CGA approved alternate connection. (The approved standard is the CGA No. 350 connection). This valve outlet is described as 1.030″ and is right-hand with external threads, with a flat seat and using a washer to seal. (See Figure 1 for an illustration of the valve outlet and mating connection). Lecture bottles have a special 5/16″-32 threads per inch, female valve outlet.

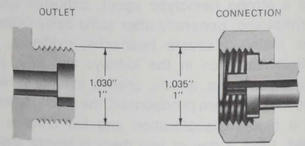


Fig. 1. CONNECTION 660 1.030″-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders containing arsine gas mixtures are not equipped with safety devices. They should, therefore, be stored away from sources of heat to avoid the development of dangerous pressures within the cylinder.

Recommended Controls

Automatic Pressure Regulators

Single stage regulator Model 3501-660 is recommended for use with Electronic Grade arsine. All metal parts in the gas stream are of stainless steel. The regulator body is of type 316 stainless steel, the diaphragm is 316 stainless steel. The regulator has a Tefzel® seat and a Model FF4374 stainless steel diaphragm packless outlet valve. The gaskets are of Teflon; there are no rubber parts. The helium leakage rate can be certified not to exceed 2×10^{-10} cm^3 per second inboard. The delivery pressure range is 0–172 kPa (0–25 psig).

Regulator Model 360-660 has a stainless steel 316 body, stainless steel 316 diaphragm, monel seat, and Kel-F® and Teflon seals for high purity. It incorporates a tied seat to assure positive shut-off. The delivery pressure range is 6.9–172.5 kPa (0–25 psig).

Flowmeters

Matheson Series 7600 laboratory, brass or stainless steel (preferably the latter) flowmeter units with 150 mm flowmeter tubes and floats or Series 7200 with flowmeter units with 65 mm tubes and a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Arsine is classified by DOT as a "Class A" poison and a flammable, compressed gas. In mixtures with nitrogen, helium, or argon it is shipped under the required "Poison Gas" and "Green" Labels. Mixtures of arsine and hydrogen are shipped under the required "Poison Gas" and "Red Gas" Labels.

Chemical Preparation

Arsine may be prepared by treating an arsenide of an electropositive metal with acids or by reduction of a sulfuric acid solution containing arsenic with an electropositive metal or electrolytically. It is also formed when arsenic trichloride is reduced in ether solution with lithium aluminum hydride. Good yields (60–90%) are obtained by decomposing a solution of sodium arsenide in liquid ammonia with ammonium bromide.

Chemical Properties

Arsine is not particularly stable and begins to decompose into its elements around 300 °C. In the presence of moisture, decomposition is affected by light. Arsine is a strong reducing agent; it can reduce silver nitrate and mercuric chloride in aqueous solution.

Arsine reacts with sodium or potassium dissolved in liquid ammonia to form $NaAsH_2$ and $KAsH_2$, respectively.

Thermodynamic and Detailed Physical Data (1)

Molecular Structure

Arsine has a trigonal structure (C_{3v} symmetry) with a H-As-H bond angle of 91.9° and an As-H bond distance of 1.519×10^{-10} m (1.519 Å).

Vapor Pressure

The vapor pressure of liquid arsine from 156.226 to 210.837 °K is represented by the following equation:

$$\log_{10} p = 28.82835 + 0.008037T - \frac{1403.32}{T} - 9.43935 \log_{10} T$$

in which p = cmHg and T = °K.

Some observed and calculated vapor pressure values are shown below:

Vapor Pressure				
Temperature, °K	kPa	mbar	Observed mmHg	Calculated mmHg
156.226	2.984	29.84	22.38	22.38
166.824	7.278	72.78	54.59	54.46
175.278	13.560	135.60	101.71	101.54
184.567	24.959	249.59	187.21	187.11
196.124	48.808	488.08	366.09	366.02
206.010	81.125	811.25	608.49	608.54
210.837	102.05	1 020.5	765.44	765.41

Latent Heat of Vaporization, ΔH_v @ −62.5 °C 16.686 kJ/mol; 51.164 kcal/kg

Thermodynamic Properties of Arsine as Ideal Gas @ 25 °C

Heat Capacity, C_p°	38.522 J/(mol·°K)
	9.207 cal/(mol·°C)
Entropy, S°	222.488 J/(mol·°K)
	53.176 cal/(mol·°C)
Free Energy Function, $F^\circ_{298} - H^\circ_0/T$	−188.506 J/(mol·°K)
	45.054 cal/(mol·°C)
Enthalpy Difference, $H^\circ_{298} - H^\circ_0$	10.201 kJ/mol
	31.278 kcal/kg
Enthalpy of Formation, ΔH_f°	66.442 kJ/mol
	203.73 kcal/kg
Free Energy of Formation, ΔF_f°	68.910 kJ/mol
	211.30 kcal/kg

ARSINE

Thermodynamic Properties of Liquid Arsine @ −62.5 °C			
Heat Capacity, C_p°	60.722 J/(mol·°K) 14.513 cal/(mol·°C)	Free Energy Function, $(F_T^\circ - H_0^\circ)/T$	31.195 cal/(mol·°C) −75.856 J/(mol·°K)
Entropy, S°	130.520 J/(mol·°K)	Enthalpy Function, $(H_T^\circ - H_0^\circ)/T$	18.130 cal/(mol·°C) 54.664 J/(mol·°K) 13.065 cal/(mol·°C)

REFERENCES

[1] For extensive tabulation of thermodynamic and physical properties, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1974*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, 1977, pp. 60–67, Matheson, Lyndhurst, New Jersey.

[3] **Ibid.**, pp. 89–91.

[4] M. B. Jacobs, *The Analytical Toxicology of Industrial Inorganic Poisons*, 1967, p. 384, John Wiley & Sons, Inc., New York, New York.

[5] **Ibid.**, pp. 377–378.

[6] **Ibid.**, pp. 374–377.

[7] *Dept. Sci. Ind. Research, Brit. Leaflet 9* (1940).

BOREON TRICHLORIDE

(Synonym: Boron Chloride)
(Formula: BCl_3)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.117 17 kg
One Mole of BCl_3	0.117 17 kg
Specific Volume @ 21.1 °C, 101.325 kPa	206.0 dm^3/kg; 3.3 ft^3/lb
Vapor Pressure @ 21.1 °C	131.7 kPa; 1.32 bar; 19.1 psia; 1.3 atm
Boiling Point @ 101.325 kPa	285.55 °K; 12.4 °C; 54.3 °F
Melting Point @ 101.325 kPa	165.85 °K; −107.3 °C; −161.1 °F
Absolute Density, Gas @ 101.325 kPa @ 0 °C	5.326 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 0 °C (Air = 1)	4.12
Density, Liquid @ 0 °C	1.372 8 kg/l
Critical Temperature	451.95 °K; 178.8 °C; 353.8 °F
Critical Pressure	3 870.6 kPa; 38.7 bar; 561.4 psia; 38.2 atm
Critical Volume	1.266 dm^3/kg
Critical Density	0.790 kg/dm^3
Critical Compressibility Factor	0.153
Latent Heat of Fusion @ −107.3 °C	2.109 kJ/mol; 504 cal/mol
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	65.655 kJ/(kmol·°K); 65.655 J/(mol·°K); 15.692 cal/(mol·°C)
@ Constant Volume	57.309 kJ/(kmol·°K); 57.309 J/(mol·°K); 13.697 cal/(mol·°C)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C Cp/Cv	1.145
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.011 35 mPa·s; 0.011 35 $mN \cdot s/m^2$ 0.011 35 cP
Viscosity, Liquid @ 0 °C	0.342 9 mPa·S; 0.342 9 $mN \cdot s/m^2$ 0.342 9 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.008 577 W/(m·°K); 20.5×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ 10 °C	0.025 2 W/(m·°K); 60.2×10^{-6} cal·cm^2/(s·cm^2·°C)
Surface Tension @ 0 °C	16.63 mN/m; 16.63 dyn/cm
Electrical Conductivity	nil
Index of Refraction, Liquid @ 5.7 °C, 486.1 nm	1.428
Coefficient of Expansion, Liquid @ 10 °C	0.001 70

Description

At room temperature and atmospheric pressure, boron trichloride is a colorless gas which fumes in the presence of moist air. It has a choking odor. It is shipped as a liquid in steel cylinders under its own vapor pressure of 30.3 kPa (4.4 psig).

Specifications

Boron trichloride is available in C.P. Grade.

Uses

Boron trichloride is used in the refining of aluminum, magnesium, zinc, and copper alloys to remove nitrides, carbides, and oxides from molten metal. It has been used successfully as a soldering flux for alloys of aluminum, iron, zinc, tungsten, and monel. Aluminum castings can be improved by treating the melt with boron trichloride vapors. Occluded gases, such as, hydrogen, nitrogen, and carbon monoxide, plus nitrides, carbides, and oxides are effectively removed by this treatment and the grain growth of the aluminum is also retarded, rendering it more uniform. Treatment of aluminum with boron trichloride improves the tensile strength and will permit the remelting of the aluminum without substantially changing the grain structure (2).

In the manufacture of electrical resistors, a uniform and

lasting adhesive carbon film can be put over a ceramic base by a process that has been developed, involving the addition of boron trichloride to benzene at high temperatures. Boron trichloride has been used for extinguishing magnesium fires in heat treating furnaces. The boron trichloride forms a magnesium chloride film that smothers the fire by preventing air from reaching the metal. Boron trichloride has been used in the field of high energy fuels and rocket propellents as a source of boron for raising the BTU value.

Boron trichloride is also used as a catalyst, and its use has been suggested in the polymerization of styrene. It is reported to yield polymers with three times the molecular weight of those produced with other catalysts tested.

Toxicity

Boron trichloride is classified as a corrosive liquid. It is corrosive to the skin and mucous surfaces because of its rapid hydrolysis to hydrochloric acid (and boric acid) by moisture. The material is generally described as much less toxic than chlorine.

Inhalation of boron trichloride vapor will result in edema and irritation of the upper respiratory tract. Skin or eye contact with liquid or vapor will cause tissue irritation.

No threshold limit value has been recommended for boron trichloride. The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 1 ppm for the related boron trifluoride and boron tribromide.

Boron trichloride is readily detectable in air by its sharp, irritating odor.

First Aid Treatments

The procedures suggested for hydrogen chloride exposures should be followed. These are described on page 379.

Precautions in Handling and Storage

1. Since boron trichloride will liberate hydrochloric acid and boric acid on contact with water or moist air, all precautions possible should be taken not to breathe the gas and to avoid contact with the skin or eyes. Chemical goggles, rubber gloves and rubber aprons should be used when working with this material. In case of contact with boron trichloride vapors or liquid, wash the contacted area with plenty of water, paying particular attention to the eyes, and get medical attention.
2. Since boron trichloride is extremely soluble in many liquids, a trap or check valve should be placed in the discharge line of a boron trichloride cylinder to prevent suckback of the material into the cylinder. Water or other material sucked back into the cylinder may cause dangerous pressures to build up, and will certainly cause an excessively corrosive condition which may lead to cylinder failure.
3. If it becomes necessary to heat a cylinder of boron trichloride it should be done in a thermostated water or oil bath.
4. Withdrawal of boron trichloride should be done in a well-ventilated area, preferably a hood.
5. Keep gas masks approved by NIOSH for acid vapors, or those with an independent oxygen or air supply, in an area not likely to be contaminated and ready for use in cases of emergency.
6. A shower and eye-bath should be conveniently located in cases of emergency.

In addition, the general rules stated in Appendix I should be observed.

Leak Detection

Leaks in boron trichloride systems can be easily detected because of the fuming vapors. After a leak has been repaired, the area around the leak should be washed and dried to remove any hydrochloric acid which may have formed. Valve leaks can usually be stopped by tightening the valve packing nut (turn clockwise as viewed from above). If leaks persist, call the supplier.

Disposal of Leaking Cylinders

Leaks in cylinders of boron trichloride which cannot be corrected may be handled in the following manner. If the cylinder is not already in a hood, it should be removed to a hood immediately. Then proceed as described under Appendix II-D for disposal of acid gases.

Materials of Construction

Detailed information regarding materials of construction suitable for use with boron trichloride is not available. Experience has shown that dry boron trichloride is noncorrosive. Boron trichloride is relatively inert to the steel containers and brass valves which are used to ship this material. The moist fumes should be handled in a material which will be resistant to corrosion by hydrogen chloride, such as copper (in the absence of air), Hastelloy B, monel, and such plastics as polyvinyl chloride, polyethylene, Teflon and Kel-F.

Cylinder and Valve Description

Boron trichloride may be shipped in any DOT approved, steel cylinder. The cylinder valve outlet used by Matheson is the Compressed Gas Association (CGA) connection No. 660 which is the alternate standard for chlorine. This valve outlet is described as 1.030 inches and is right-hand with external threads with a flat seat and using a washer to seal. (See Figure 1 for an illustration of valve outlet and mating connection). Lecture bottles have a special 5/16″-32 threads per inch female valve outlet.

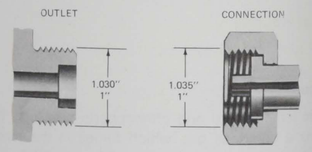


Fig. 1. CONNECTION 660 1.030″-14 RH EXT. using Flat Seat with Washer

Safety Devices

Although the DOT does not require that a safety device be used with boron trichloride, standard chlorine valves are used which may contain a safety device consisting of a fusible metal which melts at approximately 71 °C (160 °F).

Matheson

Recommended Controls

Manual Controls

Because of the low pressure of boron trichloride, adequate control can be obtained with Matheson needle valve Model 55A-660. This needle valve is made of monel bar stock and can be used for controlling the flow of boron trichloride very accurately. Monel needle valve Model 60L is available for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory monel flowmeter units with 150 mm tubes and floats are recommended for use where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

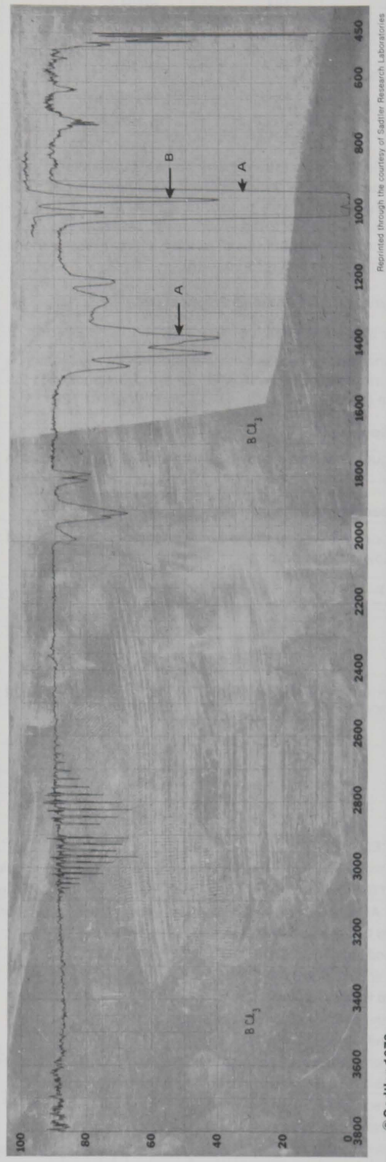
Boron trichloride is shipped under DOT regulations as a corrosive liquid, taking a "White Label."

Commercial Preparations

Boron trichloride can be prepared by any of the following methods: by chlorinating a mixture of finely divided carbon and boric oxide at 871–982 °C; by heating boric oxide with sodium, potassium, or lithium chloride at 800–1 000 °C; by heating sodium borofluoride with magnesium chloride at 500–1 000 °C.

Chemical Properties

Boron trichloride hydrolyzes rapidly with water to form hydrochloric acid and boric acid. Boron trichloride reacts with ethyl esters of hydroxy acids to give ethoxycarbonyl-substituted borates in 80–85% yields (3), ROH (R = alkyl) (1 mole) treated with 1 mole boron trichloride at −80 °C gives high yields of alkyl dichloroboronites (Cl_2BOR) (4). Boron trichloride (1 mole) and 1 mole $B(OR)_3$ (R = alkyl) at −80 °C gives high yields of Cl_2BOR. Boron trichloride reacts with chloroalcohols to give borates, chloroboronates and dichloroboronites, which disproportionate on heating (5). Boron trichloride forms addition compounds with pyridine and nitrobenzene (6). Boron trichloride at −78.5 °C forms 1:1 compounds with ethylene oxide, propylene oxide, tetrahydrofuran, and tetrahydropyran (7). Some typical reactions of boron trichloride are shown below.



Reprinted through the courtesy of Sadtler Research Laboratories
©Sadtler 1972

Fig. 2. Infrared spectrum of gaseous boron trichloride; 10 cm path length cell, with KBr windows; cell pressure: curve A:1.333 2 kPa (10 mmHg); curve B: 0.066 7 kPa (0.5 mmHg) (11)

Matheson

BCl_3 → (NH_3) → $B(NH_2)_3$
BCl_3 → (NR_3) → $ClBNR_3$
BCl_3 → (ROH) → $B(OR)_3$
BCl_3 → (H_2O) → $B(OH)_3$
BCl_3 → ($RMgX$) → R_3B

Boron trichloride reacts with monohydric phenols to give triaryl borates and aryloxyboron chlorides quantitatively. 1,-2- and 1,3-Glyols react with boron trichloride to give 1,-3, 2-dioxaborolanes and 1,3,2-dioxaborinanes, respectively.

For a review of the reactions of boron trichloride with various organic compounds see reference (8).

Thermodynamic and Detailed Physical Data

Molecular Structure (9)

The planar boron trichloride molecule has D_{3h} symmetry, a symmetry number of six with a B—Cl bond distance of 1.75 × 10^{-10} m (1.75 Å) and a Cl—B—Cl bond angle of 120°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous boron trichloride.

Vapor Pressure (10)

The vapor pressure of liquid boron trichloride is expressed by the following equation:

$$\log_{10}P = \frac{T - T_B}{T}\left[4.480 - 0.76\left(\frac{T - T_B}{T_B}\right) + 0.82\left(\frac{T - T_B}{T_B}\right)^2\right]$$

where P = atm, T = temperature (°K), and T_B = boiling point (285.55 °K).

The following values have been calculated by this equation.

Temperature, °K	Temperature, °F	Vapor Pressure kPa	atm	mbar	mmHg
213.15	−76.0	2.533	0.025	25.33	19.0
243.15	−22.0	15.908	0.157	159.05	119.3
258.15	5.0	33.235	0.328	332.37	249.3
273.15	32.0	63.733	0.629	637.28	478.0
285.55	54.3	101.325	1.000	1 013.25	760.0
293.15	68.0	132.23	1.305		
313.15	104.0	247.23	2.440		
333.15	140.0	427.49	4.219		
353.15	176.0	688.00	6.790		
373.15	212.0	1 048.7	10.35		
393.15	248.0	1 530.0	15.10		
413.15	284.0	2 162.3	21.34		
433.15	320.0	2 971.9	29.33		
451.95	353.8	3 929.4	38.78		

For vapor pressure curve, see Figure 3.

Thermodynamic Properties of Boron Trichloride As Ideal Gas @ 25 °C (9)

Heat Capacity, C_p°	62.392 J/(mol·°K); 14.912 cal/(mol·°C)
Entropy, S°	290.068 J/(mol·°K); 69.328 cal/(mol·°C)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/T$	−290.068 J/(mol·°K); −69.328 cal/(mol·°C)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	14.021 kJ/mol; 3.351 kcal/mol
Enthalpy of Formation, ΔH_f°	−402.961 kJ/mol; −96.310 kcal/mol
Free Energy of Formation, ΔF_f°	−387.982 kJ/mol; −93.908 kcal/mol

REFERENCES

[1] For extensive tabulation of the thermodynamic and physical properties of boron trichloride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1974*, Matheson, East Rutherford, New Jersey.

[2] Tullis and Ashton, *Some Developments in Aluminum Metallurgy*, Foundry Trade Journal, *1930*.

[3] Frazer and Gerrard, *J. Chem. Soc. 1955*, 2959–2960.

[4] Gerrard and Lappert, *J. Chem. Soc. 1955*, 3084–3088.

[5] Edwards, *et al*, *J. Chem. Soc. 1955*, 1470–1475.

[6] Brown and Holmes, *J. Amer. Chem. Soc.* 78, 2173–2176 (1956).

[7] Grimley, and Holliday, *J. Chem. Soc. 1954*, 1212–1215.

[8] Gerrard and Lappert, *Chem. Rev. 58*, 1081–1111 (1958).

[9] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. NSRDS-NBS-37, U. S. Government Printing Office, Washington, D. C.

[10] M. L. Iverson and S. M. Draganov in Kirk-Othmer's *Encyclopedia of Chemical Technology*, 2nd edition, *1964*, Volume 3, p. 680, John Wiley & Sons, Inc., New York, New York.

[11] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

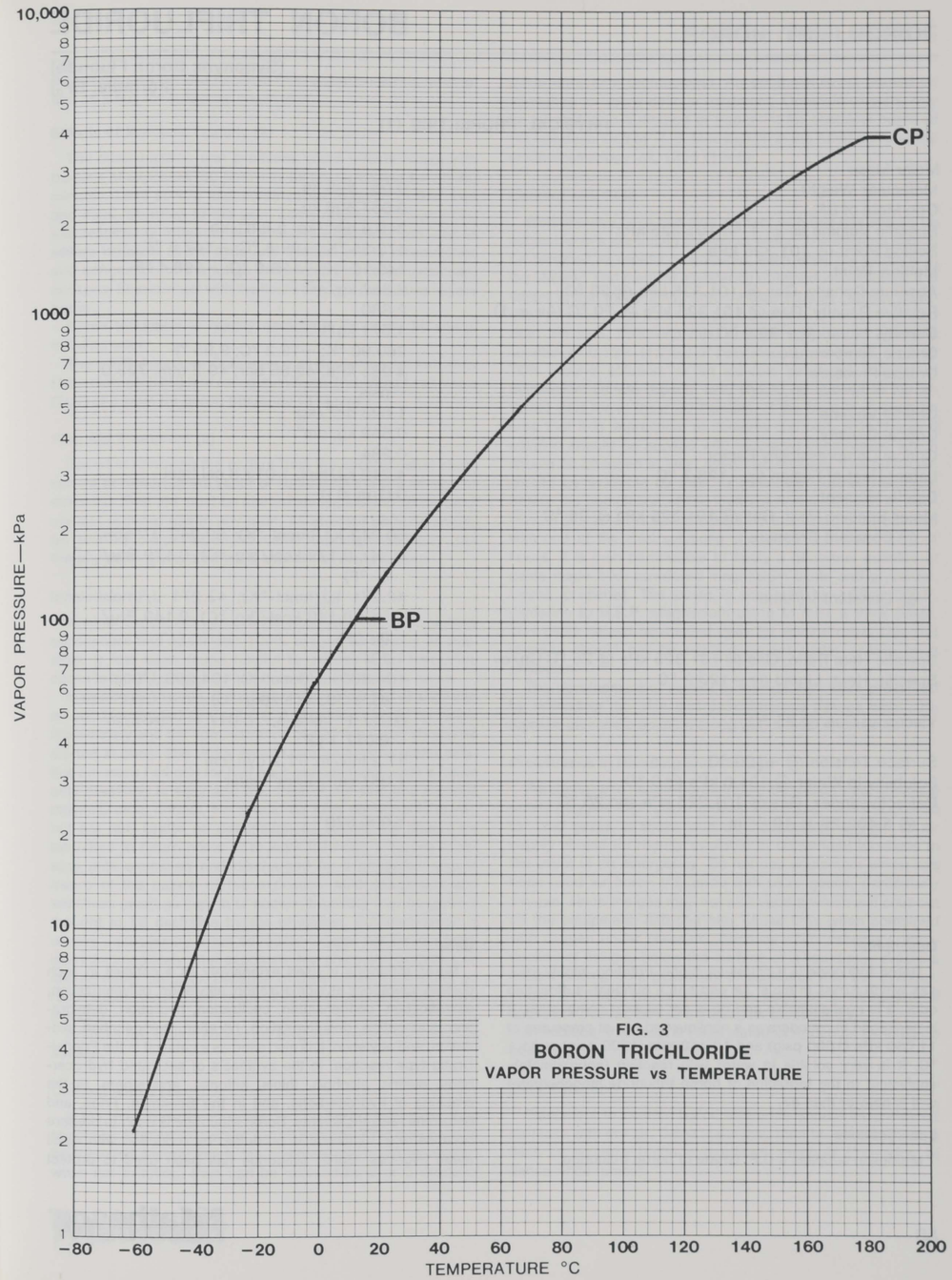


FIG. 3
BORON TRICHLORIDE
VAPOR PRESSURE vs TEMPERATURE

BORON TRIFLUORIDE

(Synonym: Boron Fluoride)
(Formula: BF_3)

PHYSICAL PROPERTIES (1)

Molar Mass	0.067 805 kg
Molecular Weight	0.067 805 kg
One Mole of BF_3	349.6 dm^3/kg; 5.6 ft^3/kb
Specific Volume @ 21.1 °C 101.325 kPa	173.35 °K; −99.8 °C; −147.8 °F
Boiling Point @ 101.325 kPa	145.15 °K; −128.0 °C; −198.4 °F
Melting Point	2.867 kg/m^3
Absolute Density, Gas @ 101.325 kPa @ 20 °C	2.380
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	1.571 kg/l
Density, Liquid @ −99.9 °C	260.90 °K; −12.2 °C; 9.95 °F
Critical Temperature	4 985 kPa; 49.85 bar; 49.2 atm; 723.0 psia
Critical Pressure	1.823 dm^3/kg
Critical Volume	0.549 kg/dm^3
Critical Density	0.284
Critical Compressibility Factor	4.242 kJ/mol; 1 013.8 cal/mol
Latent Heat of Fusion @ −128.7 °C	0 C·m; 0 D
Dipole Moment	
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	50.242 kJ/(kmol·°K); 50.242 J/(mol·°K); 0.179 kcal/(kg·°C); 0.179 Btu/lb·°F)
@ Constant Volume	42.271 kJ/kmol·°K); 42.271 J/(mol·°K); 0.149 kcal/(kg·°C); 0.149 Btu/(lb·°F)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C Cp/cv	1.201
Specific Heat, Liquid @ −123.2 °C	104.500 kJ/(kmol·K); 104.500 J/(mol·K); 0.363 kcal/(kg·°C)
Viscosity, Gas @ 25 °C	0.017 1 mPa·s; 0.017 1 mN·s/m^2 0.017 1 cP
Surface Tension @ −100 °C	17.2 mN/m; 17.2 dyn/cm
Solubility in Water @ 101.6 kPa @ 0 °C	1.057 cm^2/1 cm^3 water
Refractive Index, Gas @ 101.325 kPa and 25 °C @ 5 462.25 × 10^{-10} m	1.000 379

VAPOR PRESSURE—kPa

Description

Boron trifluoride is a colorless, highly irritating, highly toxic gas which fumes in moist air and has a pungent, suffocating odor. It is nonflammable and does not support combustion. It is packaged in cylinders as a nonliquefied gas at pressures of 11 030 kPa (1600 psig) and 12 410 kPa (1800 psig) at 21.1 °C. It is very soluble in water with reaction (approximately equivalent to the formation of boron trifluoride monohydrate) and is heavier than air.

Specifications

Matheson supplies a C.P. Grade of boron trifluoride.

Uses

Boron trifluoride is used extensively as a catalyst in such diverse operations as isomerization, alkylation, polymerization, esterification, condensation, cyclization, hydration, dehydration, sulfonation, desulfurization, nitration, halogenation, oxidation, and acylation. It is also used as a catalyst in the Friedel-Crafts type reaction, in the synthesis of saturated hydrocarbons, olefins, alcohols, thiols, ketones, and ethers, in the cracking of hydrocarbons, and in the Beckman, Fries, and benzidine rearrangements. Boron trifluoride is used to prepare boranes, e.g., diborane is produced by reduction with alkali metal hydrides. Boron trifluoride has been used to protect

Matheson

molten magnesium and its alloys from oxidation during casting, and as a flux for soldering magnesium.

Effects of Man and Toxicity (2)

The concentration that produces acute effects varies with the time of exposure; 50 ppm may be fatal if inhaled for 30–60 minutes. Less severe exposures cause irritation of the nose and eyes, smarting of the skin, some degree of conjunctival and respiratory irritation. More severe exposures can lead to severe irritation of the eyes and eyelids and to inflammation and congestion of the lungs and circulatory (cardiovascular) collapse. Skin contact with the liquid or vapor can cause severe burns.

Boron trifluoride is readily detectable in air by its sharp, irritating odor.

The 1979 American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a Threshold Limit Value (TLV) of 1 ppm for boron trifluoride (3 mg/m^3).

First Aid Treatment (2)

Speed in removing the patient from the contaminated atmosphere or removing the vapor or liquid from the skin or eyes is essential. First aid must be started immediately in all cases of contact with the gas in any form. All affected persons should be referred to a physician, no matter how slight the injury, and the physician given a detailed account of the accident.

Inhalation

In minor exposures, remove the victim to an uncontaminated atmosphere and administer 100% oxygen as quickly as possible. It has been found helpful to expose even borderline cases to 100% oxygen at half hour intervals for 3–4 hours.

In severe exposures, the worker must be carried at once into an uncontaminated atmosphere. A physician should be called immediately and the administration of 100% oxygen should be started at once. The victim should receive oxygen under positive pressure (<4 cm) for half hour periods for at least 6 hours until breathing is easy and the color of the skin and mucous membranes is normal. He should be kept comfortably warm, but not hot. Under no circumstances should the patient be permitted to return home or to work following a severe exposure until examined and discharged by a physician who is aware of the nature of the exposure. Mild analgesics and sedatives (such as aspirin or sodium bromide) may be given if thought to be desirable by the physician, but medication is usually unnecessary when adequate oxygen has been administered immediately after exposure. Morphine and barbiturates should never be given because of their depressant effect on respiration. Cardiac and respiratory stimulants are not recommended.

Artificial respiration should not be given unless breathing has ceased.

Contact with Eyes

If the eyes have been contacted by boron trifluoride, they should be flushed with water for 15 minutes. This may have to be repeated several times. Ice compresses should be applied when not irritating. Pain can be relieved by 2 or 3 drops of 0.5% tetracaine (pontocaine). An ophthalmologist should be consulted for more definite treatment. Ophthalmologists may be interested in a method of treatment for chemical burns of the eye described by R. S. McLaughlin in the American Journal of Ophthalmology 29, 1355 (1946).

Contact with Skin

Workers who have had skin contact with this gas should be subjected to a drenching shower of water. The clothing should be removed as rapidly as possible, even while the victim is in the shower, and medical assistance obtained immediately. It is essential that the affected area be washed with copious quantities of water for a sufficient period of time to remove all acid from the skin. Following this, an iced aqueous or alcoholic solution of 0.13% (1:750) of benzalkonium chloride, an iced 70% alcohol solution, or an ice-cold saturated solution of magnesium sulfate (Epsom salt) should be applied to the affected part for at least 30 minutes. If the burn is in such an area that it is impractical to immerse the part, then the iced solution should be applied with saturated compresses which should be changed at least every two minutes. The physician should be available by then to administer further treatment before the completion of the iced solution treatment. If, however, a physician is not available by that time, the treatment with one of the iced solutions should be continued for 2–4 hours. It is then permissible to apply a generous quantity of paste made from powdered magnesium oxide and glycerine, freshly prepared. The paste is prepared by adding U.S.P. glycerine to U.S.P. magnesium oxide to form a thick paste. This paste should be applied daily for several days. Oils and greases should not be applied except under orders by a physician.

The development of severe burns has also been prevented by infiltrating the skin and subcutaneous tissues with 10% calcium gluconate solution along with a local anesthetic.

Precautions in Handling and Storage

Personnel who handle boron trifluoride should wear chemical safety goggles and rubber gloves. Also, gas masks approved for acid gases or those with an independent oxygen or air supply should be readily available in convenient locations in the event of an emergency. Do not use equipment which has been used for boron trifluoride with other gases, particularly oxygen, since the gas may have oil vapors which will coat out on the equipment, and this may cause fires when combined with oxygen under pressure. Because of its reactivity, introduction of the gas below the surface of a liquid may create a hazard arising from possibility of suckback into the cylinder. Traps or check valves should be used as a safeguard. If suckback occurs, advise the supplier immediately.

In addition, the general rules stated in Appendix I should be observed.

Leak Detection

Equipment to contain boron trifluoride should be pretested for leaks with dry air. Small leaks may then be detected with a flash or squeeze bottle of aqueous ammonia (formation of dense white fumes).

Matheson

Cylinder valve leaks can usually be corrected by tightening the valve packing nut (turn clockwise as viewed from above). If valve leaks persist or leaks appear at any portion of the cylinder, advise the supplier immediately.

Disposal of Leaking Cylinders

Leaking cylinders of boron trifluoride which cannot be corrected may be handled in the following manner: If the cylinder is not already in a hood, it should be removed to a hood immediately. Then proceed as described under Appendix II-D for disposal of acid gases.

Materials of Construction

Materials of construction recommended for the handling of dry boron trifluoride are steel tubing or pipe, stainless steel, copper, nickel, monel, brass, and aluminum, and the more noble metals. These metals will stand up adequately to at least 200 °C. Pyrex glass is also suitable up to about 200 °C at low pressures. For moist gas the following materials of construction are recommended: copper, Saran tubing, hard rubber, paraffin wax and Pyrex glass show fair resistance. Plastic materials, such as Teflon, Epons, polyethylene, and pure polyvinyl chloride are not attacked at 80 °C. Rubber tubing, phenolic resins, nylon, cellulose, and commercial polyvinyl chloride are readily attacked.

Cylinder and Valve Description

Boron trifluoride is usually shipped in cylinders having a DOT specification calling for a minimum design pressure of 13 790 kPa (2 000 psig). Cylinder valves have been constructed of steel having stainless steel stems with silver seats. A valve that is becoming more popular because it is less subject to freezing and corrosion (used by Matheson) is one constructed of an aluminum-iron-bronze alloy having a monel stem containing a Kel-F seat. This valve is Teflon packed. The valve outlet designated as standard by the Compressed Gas Association (CGA) is valve outlet No. 330. The outlet and its accompanying connection are shown in Figure 1. The outlet is of 0.825 inch diameter, left-hand external with flat seat, using a washer to seal. Lecture bottles have a special 5/16"-32 threads per inch, female valve outlet.

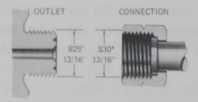


Fig. 1. CONNECTION 330 .825"-14 LH EXT. used with Flat Seat and Washer

Safety Devices

DOT approved cylinders containing boron trifluoride require safety devices approved by the Bureau of Explosives. Boron trifluoride cylinders are required to have a safety device consisting of a frangible disc which is backed up with a fusible metal melting at either 73.9 °C (165 °F) or 100 °C (212 °F). If cylinders are over 55" long, exclusive of the neck, two safety devices, one at each end, are required. The purpose of this safety device is to relieve the cylinder contents before the bursting pressure of the cylinder is reached. This type of safety device requires heat to melt the fusible metal, allowing the frangible disc to function properly when excessive pressures are built up.

Recommended Controls

Automatic Pressure Regulators

Two single stage regulators are available for use with boron trifluoride. They are designated as Models B15B-330 and B16B-330 and differ only in their delivery pressure ranges which are 28-345 kPa (4-50 psig) and 345–4 480 kPa (50-650 psig), respectively. The regulators have chemically coated nickel bodies and internal parts constructed of monel. The diaphragms are Kel-F backed with silver-plated nickel-silver alloy and the seats are Kel-F. The regulators are equipped with gauges having monel Bourdon tubes to indicate cylinder and delivery pressure. The outlets of the regulators are equipped with monel needle valves for fine flow control, and hose end connections are supplied as a separate accessory.

Manual Controls

A manual flow control valve designated as Model 55A-330 is also available for intermittent flow control directly from the cylinder in cases where constant attention will be given by an individual using the gas. Such a manual flow control valve will not effectively control pressure and should not be used where pressure control is essential. Monel needle valve Model 60L is recommended for lecture bottles.

Flowmeters

Matheson Series 7600 monel flowmeter units with 150 mm flowmeter tubes and floats, of the rotameter type, are recommended where definite flow rates must be measured. Monel electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

Matheson Series 8260 of monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ±1.2%.

Shipping Regulations

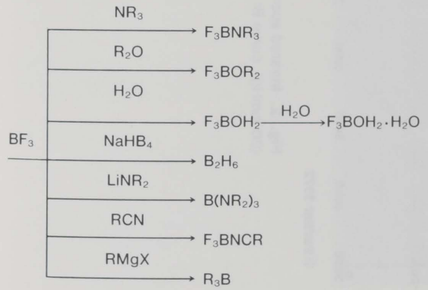
Boron trifluoride is shipped under DOT regulations as nonflammable, compressed gas taking a "Green Label".

Commercial Preparations

In the present commercial preparation of boron trifluoride, borax is slowly added to hydrofluoric acid to yield water and $Na_2O \cdot (BF_3)_4$, or boric acid is treated with ammonium bifluoride to yield water, ammonia, and the compound $(NH_4)_2O \cdot (BF_3)_4$. The boron trifluoride complex or "fluoborax" is transferred to a generator and is treated with cold fuming sulfuric acid. The reaction mass is slowly heated and the generation of boron trifluoride is controlled by regulating the temperature. Boron trifluoride is also produced commercially by treating fluorosulfonic acid with boric acid.

Chemical Preparation

1. With elements: alkali and alkaline earth metals reduce boron trifluoride to elemental boron and the metal fluoride. Gaseous or liquid boron trifluoride does not react with mercury or chromium, even at high pressures for long periods. Red-hot iron is not attacked by boron trifluoride.
2. With oxides: When boron trifluoride is allowed to react with slaked lime, calcium borate and fluoborate are formed with evolution of heat. With anhydrous calcium oxide or magnesium oxide, the metal fluoride and the volatile boron oxyfluoride are formed.
3. With halides: BCl_3 and BF_3 do not react when heated to 500 °C. Aluminum chloride or aluminum bromide react with boron trifluoride when gently heated to give the corresponding boron halide and aluminum fluoride. Boron trifluoride forms no coordination compounds when passed at 1 atmosphere over the solid chlorides of copper, silver, or potassium at temperatures from −75 °C to 530 °C.
4. Alkyl borines: Some alkyl borines have been prepared by passing dry boron trifluoride into the appropriate alkyl Grignard reagent followed by distillation in a nitrogen atmosphere.
5. Aryl Borines: These compounds have been prepared similarly to the alkyl borines.
6. As a catalyst: Boron trifluoride, being electrophilic, acts as an acid catalyst. Boron trifluoride catalyzes numerous types of reactions, viz., esterification, nitrations, oxidations, reductions, halogenations, etc.
7. Boron trifluoride forms molecular compounds with many diverse classes of compounds, e.g., alcohols, ethers, acid anhydrides, ketones, aldehydes, and amines. Also, hydrogen sulfide, sulfur dioxide, mercaptans, and alkyl form 1:1 molecular complexes.
8. Some typical reactions of boron trifluoride are shown below.



Thermodynamic and Detailed Physical Data
Molecular Structure

Boron trifluoride has a planar structure with D_{3h} symmetry, a symmetry number of 6 with a B—F bond distance of 1.307 × 10^{-10} m (1.307 Å) and an F—B—F bond angle of 120°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous boron trifluoride.

Vapor Pressure (3)

The vapor pressure of liquid boron trifluoride over the temperature range of −127.3 °C to 98.2 °C is expressed by the following equation:

$$\log_{10} p = 7.13299 \frac{-588.043}{T - 34.951}$$

in which p = mmHg and T = °K

Some vapor pressure values calculated by this equation are shown below.

Temperature °K	Temperature °C	Vapor Pressure kPa	Vapor Pressure mbar	Vapor Pressure mmHg
145.85	−127.30	8.89	88.9	67.7
152.65	−120.50	18.29	182.9	137.1
160.75	−112.40	38.33	383.3	287.5
167.85	−105.30	68.10	681.0	510.8
171.15	−120.00	87.18	871.8	653.9
173.25	−99.90	101.39	1 013.9	760.5

Some vapor pressure values above 1 atm are shown below. They have been calculated by the equation $\log_{10} p = 5.1009 - 889.6$ in which p = atm and T = °K (4).

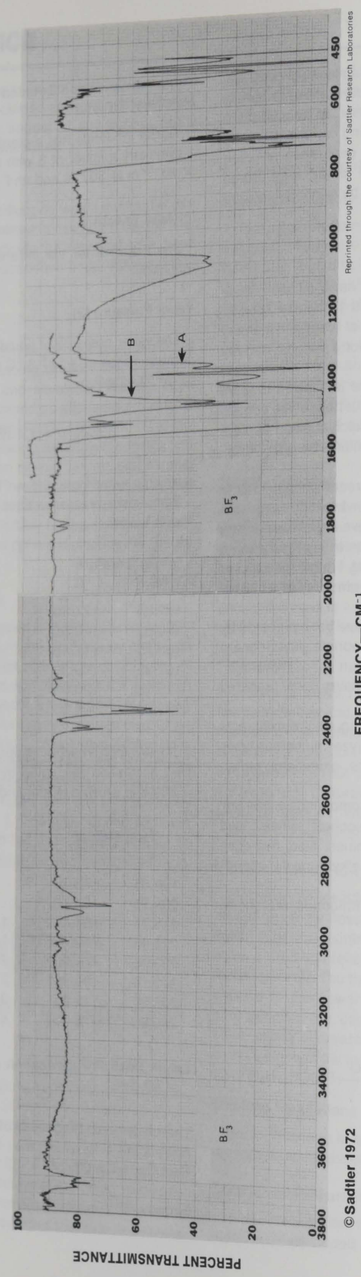
Temperature °K	Temperature °C	Vapor Pressure kPa	Vapor Pressure bar	Vapor Pressure atm
199.85	−73.30	452.2	4.522	4.463
209.85	−63.30	736.9	7.369	7.273
218.75	−54.40	1 096	10.96	10.82
223.90	−49.25	1 360	13.60	13.42
233.95	−39.20	2 014	20.14	19.88
243.19	−29.96	2 830	28.30	27.93
253.20	−19.95	3 921	39.21	38.70
260.90	−12.25	4 975	49.75	49.10

Latent Heat of Vaporization @ − 99.9 °C	16.974 kJ/mol 4.057 kcal/mol

Thermodynamic Properties of Boron Trifluoride as Ideal Gas @ 25°C (5)

Heat Capacity, C_p°	50.446 J/(mol·°K) 12.057 cal/(mol·°C)
Entropy, S°	254.245 J/(mol·°K) 60.766 cal/(mol·°C)

Matheson



Reprinted through the courtesy of Sadtler Research Laboratories

©Sadtler 1972

Fig. 2. Infrared spectrum of gaseous boron trifluoride; 10 cm path length cell, with KBr windows; cell pressure: curve A: 2.666 (20 mmHg), curve B: 0.066 7 (0.5 mmHg) (6).

Free Energy Function, ($F^{\circ}_{298} - H^{\circ}_{298}$)/T	−254.245 J/(mol·°K) −60.766 cal/(mol·°C)	**Enthalpy of Formation, ΔH°_{f}**	−1 135.621 kJ/mol −271.420 kcal/mol
Enthalpy Difference $H^{\circ}_{298} - H^{\circ}_{0}$	11.648 kJ/mol 2.784 kcal/mol	**Free Energy of Formation, ΔF°_{f}**	−1 119.019 kJ/mol −267.452 kcal/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of boron trifluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1974*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment, 2nd edition, 1977*, pp. 83–87, Matheson, Lyndhurst, New Jersey.

[3] H. S. Booth and J. M. Carter, *J. Phys. Chem. 36*, 1359 (1932).

[4] A. Eucken and E. Schroeder, *Z. Phys. Chem. B 41*, 307–319 (1938).

[5] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[6] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

BROMINE PENTAFLUORIDE

(Formula: BrF_5)

PHYSICAL PROPERTIES (1)

Molar Mass	0.174 896 kg
Molecular Weight	0.174 896 kg
One Mole of BrF_5	43.77 kPa; 437.7 mbar; 6.348 psia; 0.43 atm
Vapor Pressure @ 20 °C	314.05 °K; 40.9 °C; 105.6 °F
Boiling Point @ 101.325 kPa	212.55 °K; −60.6 °C; −77.1 °F
Freezing Point	2.481 2 kg/l
Density, Liquid @ 20 °C	7.280 kJ/mol; 1.740 kcal/mol
Latent Heat of Fusion @ −60.6 °C	1.355 4
Index of Refraction, Liquid @ 101.325 kPa, n_D @ 20 °C	7.76
Dielectric Constant, Liquid @ 25 °C	$91.0 \times 10^{-9}\ \Omega^{-1}/cm$
Specific Conductivity @ 25 °C	23.2
Trouton's Constant	

VAPOR PRESSURE, kPa

Description

At room temperature bromine pentafluoride is a pale yellow liquid. It has a high Trouton's constant, 23.2, indicating that it is somewhat associated in the liquid state. Molecular weight determinations indicate that there is no association in the vapor state. Bromine pentafluoride is a very stable compound, showing no signs of decomposition up to 460 °C. It is normally shipped in compressed gas cylinders under its own vapor pressure. It cannot be considered a compressed gas, because of its low pressure.

Bromine pentafluoride is an extremely reactive material in that it reacts with every known element except the inert gases, nitrogen, and oxygen. It will react, under proper conditions with a vast majority of inorganic compounds, with the exception of the inorganic fluorides. It will attack organic compounds vigorously even under mild reaction conditions. However, the reactions are often explosive and are of little preparative value.

Specifications

Bromine pentafluoride is supplied in a minimum purity of 98.0%. Probably impurities are air, carbon tetrafluoride, and a fractional percent of hydrogen fluoride.

Uses

Its major use is as a fluorinating agent. It is also of interest as a propellent for rockets and missiles.

Effects In Man and Toxicity (2)

Bromine pentafluoride is a pulmonary irritant and can cause pulmonary edema. It can cause severe chemical and thermal burns. Exposure to high concentrations is usually fatal, respiratory damage and pulmonary edema being the cause of death. Prolonged exposure to as little as 5–10 ppm causes irritation of the eyes and nasal and buccal mucosa. Direct contact with the skin can cause severe burns in 0.2 second and an exposure of 0.6 second can result in thermal flash burns comparable with those produced by an oxyacetylene flame.

The 1979 American Conference of Governmental Industrial Hygienists (ACGIH) has established a Threshold Limit Value (TLV) of 0.1 ppm (0.7 mg/m^3) for bromine pentafluoride.

Bromine pentafluoride provides adequate warning of its presence by its sharp, pentrating odor.

First Aid Treatment (2)

The first aid treatment to be followed is that described for hydrogen fluoride, see page 379.

Precautions in Handling and Storage

Because of the corrosive nature of bromine pentafluoride, it should be handled with extreme care. Anyone using this material should wear suitable protective clothing such as neoprene gloves, aprons, and face shields. Air line or oxygen masks are recommended for protection against vapor only. An instant-acting safety shower should be available in the general area where bromine pentafluoride is handled along with several filled buckets of sodium bicarbonate and a reserve supply to absorb any spillage. Dry-type fire extinguishers using sodium bicarbonate can be used safely to dispose of spillage, as well as combat any secondary fires. An eye-fountain should also be located in the general area.

In addition, the general rules listed in Appendix I should be observed.

Materials of Construction

Bromine pentafluoride can be used with a variety of metals due to the formation of a passive metal fluoride film which protects the metal from further corrosion. Monel and nickel are preferred materials of construction; however, metals such as copper, brass, and steel may also be used. Highly fluorinated polymers such as Kel-F and Teflon are resistant to liquid and vapor at ordinary temperatures under normally static conditions only. Their use in flow conditions is not recommended. Material suitable for gaskets are soft copper, 2S aluminum, lead, and Teflon, plain or impregnated with a high percentage of calcium fluoride. Braided copper or Teflon can be used for valve packings. A pipe thread lubricant, if needed, should be a water dispersion of Teflon, put on in two or three applications before assembling.

It is of the utmost importance that all equipment used in bromine pentafluoride service be thoroughly cleaned to remove grease, scale, pipe dope, or other contaminants. All equipment should be disassembled, degreased, and reassembled with proper packing before use. Degreasing and cleaning should be done with a nonaqueous solvent such as acetone, trichloroethylene, or carbon tetrachloride. After cleaning, the system should be thoroughly purged with a stream of dry nitrogen. Since the corrosion resistance of the materials of construction recommended depends on the formation of a passive fluoride film, a passivating procedure should be used after the cleaning and drying procedure mentioned above. This procedure consists of slowly displacing the dry nitrogen from the system by bleeding a small amount of bromine pentafluoride through the system. Because of the very low vapor pressure of bromine pentafluoride it is recommended the system be evacuated and bromine pentafluoride vapors bled slowly into the system and left for about 30 minutes to ensure that a passive film has been built up. The system can then be purged with dry nitrogen, and is ready for use.

Cylinder and Valve Description

The valve outlet designated as Compressed Gas Association (CGA) No. 670 which has a thread size of 1.030 inches and is a left-hand with external threads is the approved standard. The

CONNECTION 670 1.030"-14 LH EXT. using Flat Seat with Washer

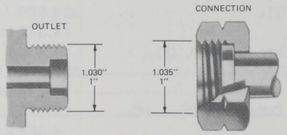


Fig. 1.

mating connection seats on a flat washer. Figure 1 illustrates the valve outlet and the mating connection used in this service.

Safety Devices

Since bromine pentafluoride is not equipped with safety devices care should be taken to see that the cylinder is not overheated. Although bromine pentafluoride is a liquid, excessive temperatures over 51.7 °C (125 °F) may cause it to expand, completely filling the cylinder, and creating dangerous hydrostatic pressures.

Recommended Controls

Since bromine pentafluoride is a liquid, its regulation from the cylinder can be effected by a manual needle valve. Matheson provides a Model 55A-670 monel needle valve for direct connection to a cylinder. This needle valve can be provided with ¼" compression fitting, ¼" male or female NPT aside from the usual serrated hose end.

Shipping Regulations

Bromine pentafluoride is shipped under DOT regulations in approved cylinders for shipment of compressed gases. It is shipped as a corrosive liquid, taking a "White Acid Label".

Commercial Preparation

Bromine pentafluoride is prepared by direct combination of 1 part bromine with 5 parts fluorine in copper apparatus at 200 °C. It can also be prepared by heating a mixture of bromine trifluoride and fluorine to 200 °C.

Chemical Properties

Bromine pentafluoride is a powerful fluorinating agent. Metal chlorides, bromides, and iodides are converted to fluorides by treatment with bromine pentafluoride. It will react vigorously with water to give bromine, oxygen, and bromic and hydrofluoric acids.

Bromine pentafluoride will convert many oxides to fluorides and oxyanions to fluoanions. Bromine pentafluoride will react with sulfur, selenium, tellurium, phosphorus, arsenic, antimony, silicon, and boron at room temperature or at slightly elevated temperatures to give the corresponding fluoride.

Ether, benzene, and turpentine will burn immediately on contact with bromine pentafluoride. Methyl chloride reacts with it with explosive violence. Carbon tetrachloride is relatively inert to bromine pentafluoride at ambient temperatures. The reactions of bromine pentafluoride are frequently explosive and find little preparative use.

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

The bromine pentafluoride molecule has a tetragonal pyramid structure, with C_{4v} symmetry, with a symmetry number of four. It has four long Br-F bonds with a bond distance of 1.79×10^{-10} m (1.79 Å) and one short Br-F bond with a bond distance of 1.68×10^{-10} m (1.68 Å). The bond angles $F^{equatorial}$-Br-$F^{equatorial}$ and F^{axial}-Br-$F^{equatorial}$ are close to 90°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous bromine pentafluoride.

Density (4)

The density of liquid bromine pentafluoride between 15 and 76 °C is expressed by the following equation.

$$d_L = 2.5509 - 0.003\,484t - 3.45 \times 10^{-6}t^2$$

in which d = kg/dm^3 and t = °C.

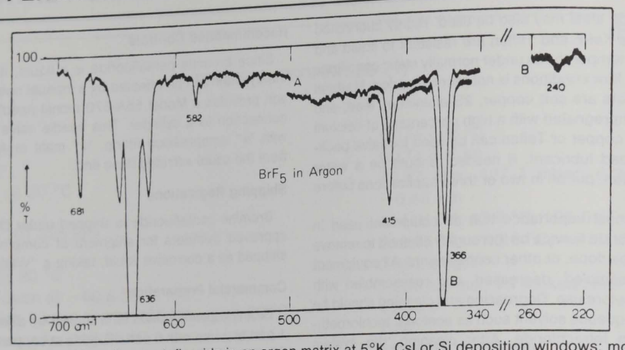


Fig. 2. Infrared spectrum of bromine pentafluoride in an argon matrix at 5°K, CsI or Si deposition windows; monomer bands are denoted by their frequencies; dimer bands are present at 648, 623, 578, and 522 cm^{-1} (8).

Some density values calculated by this equation are shown below:

Temperature, °C	d_L = kg/dm³
1	2.547
5	2.533
10	2.516
20	2.480
30	2.443
40	2.406
50	2.368
60	2.329
70	2.290

Vapor Pressure (5)

The vapor pressure of liquid bromine pentafluoride between −42.5 and 60 °C is represented by the following Antoine vapor pressure equation:

$$\log_{10} = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C and the constants A, B, and C, have values of 7.608 4, 1 385.6, and 252.2, respectively.

Some vapor pressure values are shown below:

Temperature, °C	Vapor Pressure kPa	mbar	mmHg
−42.50	1.333	13.33	10
−32.50	2.666	26.66	20
−21.50	5.333	53.33	40
−14.50	7.999	79.99	60
−9.30	10.67	106.7	80
−5.30	13.33	133.3	100
8.90	26.66	266.6	200
17.80	40.00	400.0	300
24.60	53.33	533.3	400
30.00	66.66	666.6	500
34.70	79.99	799.9	600
38.70	93.30	933.0	700
40.90	101.325	1 013.25	760
42.30	106.66	1 066.6	800
45.50	119.99	1 199.9	900
48.50	133.32	1 333.2	1 000
55.70	160.00	1 600.0	1 200
60.30	200.00	2 000.0	1 500

For vapor pressure curve, see Figure 3.

Thermodynamic Properties of Bromine Pentafluoride as Ideal Gas @ 25 °C (3)

Heat Capacity, C_p°	101.403 J/(mol·°K)
	24.236 cal/(mol·°C)
Entropy, S°	323.578 J/(mol·°K)
	74.337 cal/(mol·°C)
Free Energy Function, $(F^\circ_{298} - H^\circ_{298})/T$	−323.578 J/(mol·°K)
	−74.337 cal/(mol·°C)
Enthalpy Difference, $H^\circ_0 - H^\circ_{298}$	−19.179 kJ/mol
	4.584 kcal/mol
Enthalpy of Formation, ΔH_f°	−428.718 kJ/mol
	−102.466 kcal/mol
Free Energy of Formation ΔF_f°	−351.410 kJ/mol
	−83.989 kcal/mole
Standard Heat of Formation, Liquid @ 101.325 kPa (6) @ 25 °C	−458.566 kJ/mol
	−109.6 kcal/mol
Free Energy of Formation, Liquid @ 101.325 kPa (6) @ 25 °C	−351.87 kJ/mol
	−84.1 kcal/mol
Entropy, Liquid @ 101.325 kPa (6) @ 25 °C	225.1 J/mol
	53.8 cal/mol

Matheson

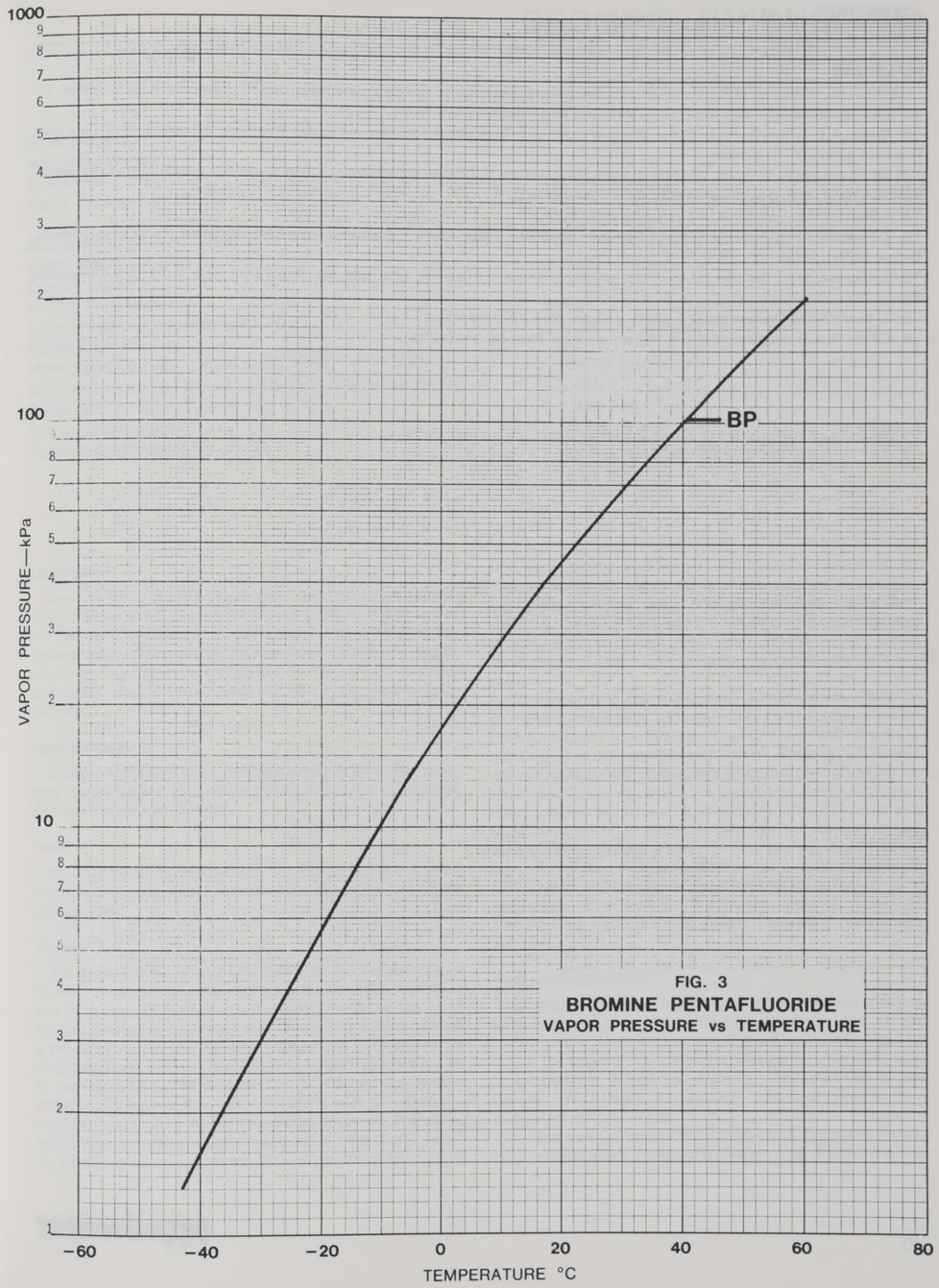


FIG. 3
BROMINE PENTAFLUORIDE
VAPOR PRESSURE vs TEMPERATURE

BROMINE PENTAFLUORIDE

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of bromine pentafluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1974*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 47-51, Matheson, Lyndhurst, New Jersey.

[3] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[4] A. A. Banks and J. J. Maddock, *J. Chem. Soc. 1955*, 2779.

[5] B. J. Zwolinski, *et al.*, *Selected Values of Chemical Compounds, 1968*, Volume 1, Thermodynamics Research Center, Texas A&M University, College Station, Texas.

[6] D. D. Wagman, *et al.*, *Selected Values of Chemical Thermodynamic Properties, 1968*, Natl. Bur. Stand. Tech. Note 270-3, U. S. Government Printing Office, Washington, D. C.

[7] G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys. 42*, 2236 (1965).

[8] R. A. Frey, R. L. Redington, and A. L. K. Aljibury, *J. Chem. Phys. 54*, 344 (1971).

BROMINE TRIFLUORIDE

(Formula: BrF_3)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.136 899 kg
One Mole of BrF_3	0.136 899 kg
Vapor Pressure @ 20 °C	0.931 kPa; 0.009 3 bar; 0.135 psia; 0.009 2 atm
Boiling Point @ 101.325 kPa	398.90 °K; 125.75 °C; 258.4 °F
Triple Point	281.92 °K; 8.77 °C; 47.79 °F
Density Liquid @ 25 °C	2.803 kg/l
Critical Temperature	600 °K; 327 °C; 620.6 °F
Latent Heat of Fusion @ 8.77 °C	12.027 kJ/mol; 2 874.6 cal/mol
Dipole Moment, Gas	3.97×10^{-30} C·m; 1.19 D
Molar Specific Heat, Liquid @ 27.4 °C	124.73 J/(mol·°K)
Index of Refraction, Liquid @ 101.325 kPa, n_D @ 25 °C	1.453 6
Dielectric Constant, Gas @ 142.4 °C	1.003 748
Trouton's Constant	25.7
Specific Conductivity @ 25 °C	$8.0 \times 10^{-3}\ \Omega^{-1}$/cm

Description

Bromine trifluoride is a highly toxic, colorless to gray-yellow liquid, having the highest boiling point (125.75 °C) of any of the halogen fluorides. It is extremely reactive, forming the highest known fluorides of the elements from their halides. Bromine trifluoride etches glass and quartz, sets fire to paper and wood, and will react violently with most organic compounds.

Specifications

Bromine trifluoride has a minimum purity of 98%. The probable impurities are air, carbon tetrafluoride, and a fractional percent of hydrogen fluoride.

Uses

Bromine trifluoride is used as a fluorinating agent and as an electrolytic solvent, and is of interest as a propellant for rockets and missiles.

Toxicity

The toxic effects of bromine trifluoride are comparable to those of chlorine trifluoride, which is considered the most toxic and hazardous of the halogen fluorides. The properties of all the halogen fluorides are such that there is little difference from a practical standpoint. Extreme caution and care should be observed when working with bromine trifluoride, since it can be considered a highly toxic material, comparable to chlorine trifluoride. When handling this material the rules governing the handling of chlorine trifluoride should be observed. Therefore, by analogy, the 1979 ACGIH Threshold Limit Value of 0.1 ppm by volume in air is suggested. Concentrations of 50 ppm or more may be fatal in 30 minutes to 2 hours. In concentrations of 100 ppm toxicity symptoms were noticed after 3 minutes in experimental animals, and at 500 ppm symptoms appeared at once; i.e., gasping for breath, swelling of eyes and eyelids, cloudiness of the cornea, lacrimation, severe salivation, and acute distress. Death was preceded by convulsions in many cases.

From a practical standpoint, fatal concentrations would be so irritating to the eyes and respiratory tract that this concentration could not be tolerated. Although the threshold odor is quite low, it is not quantitatively known. Toxic symptoms will appear more slowly in low concentrations, but in all cases where the TLV is exceeded, the symptoms of eye and respiratory irritation will appear. Contact of bromine trifluoride with body tissue will result in severe damage. The vapors are also very corrosive. Severe irritation of the eyes, resulting in blindness or ulceration, has been observed as a result of exposure to the vapor. In the exposure of experimental animals to concentrations higher than the TLV, severe nephrosis as well as marked toxic hepatosis and severe respiratory involvement occurred.

First Aid Suggestions

Summon a physician immediately for any person who has been burned or overcome by bromine trifluoride.

Prior to the physician's arrival, first aid measures should be taken. Those presented herein are based upon what is believed to be common practice in industry. Their adoption in any specific case should be subject to prior endorsement by a competent medical advisor.

1. Remove exposed victim from the area. For exposure due to inhalation given artificial respiration only if breathing has

ceased. Oxygen should be administered by trained personnel only.

2. For external exposure wash with large amounts of water and follow with lime water. Remove any affected clothing.
3. Follow recommended first aid for hydrofluoric acid.
4. In all cases get immediate medical attention.

Precautions in Handling and Storage

1. Since bromine trifluoride is so extremely corrosive to human tissue and the eyes, personnel working with this material should wear clean rubber gloves, safety glasses, a face shield, and a protective apron.
2. Work should be done in a well-ventilated area, preferably a hood with forced ventilation.
3. In removing the contents from a cylinder, attach a suitable needle valve to the valve outlet so that uniform rates of flow can be controlled. Dry nitrogen may be used to pressurize the cylinder in order to transfer the liquid.
4. The cylinder should never be directly connected to a container of liquid, since suckback may occur causing a violent reaction within the cylinder. To prevent suckback, a trap, check valve, or vacuum break should be inserted in the line. The trap should be of sufficient size to take the total liquid volume that can be sucked back.
5. An instant-acting safety shower should be available, as well as filled buckets of sodium bicarbonate and a reserve supply to absorb any spillage. Dry-type fire extinguishers using sodium bicarbonate can be used to dispose of spillage as well as combat secondary fires.
6. An air-line respirator or oxygen mask should be kept close by the operation site, in an area that is not likely to become contaminated, to be used in case of emergency where dangerous concentrations may exist.

In addition, the general rules listed in Appendix I should be observed.

Materials of Construction

Bromine trifluoride can be used with a variety of metals due to the formation of a passive metal fluoride film which protects the metal from further corrosion. Monel and nickel are the preferred materials of construction; however, metals, such as copper, brass and steel may be used. Highly fluorinated polymers such as Kel-F and Teflon are resistant to liquid and vapor at ordinary temperatures under normally static conditions only. Their use in flow conditions is not recommended. Materials suitable for gaskets are soft copper, 2S aluminum, lead, and Teflon plain or impregnated with a high percentage of calcium fluoride. Braided copper backed with Teflon can be used for valve packings. A pipe thread lubricant, if needed, should be a water dispersion of Teflon, put on in two or three applications, allowing the threads to dry between applications before assembling.

It is of utmost importance that all equipment used in bromine trifluoride service be thoroughly cleaned to remove grease, scale, pipe dope, or other contaminants. All equipment should be disassembled, degreased and reassembled with proper packing before use. Degreasing and cleaning should be done with a nonaqueous solvent such as acetone, trichloroethylene, or carbon tetrachloride. After cleaning, the system should be thoroughly purged with a stream of dry nitrogen. Since the corrosion resistance of the materials of construction recommended depends on the formation of a passive fluoride film, a passivating procedure should be used after cleaning and drying the system as mentioned above. This procedure consists of evacuating the dry nitrogen from the system and slowly bleeding a small amount of bromine trifluoride vapor into the system. Because of the very low vapor pressure of bromine trifluoride it is recommended that the vapor be left in the system for about an hour to ensure that a passive film has been built up. The system can then be vented and is ready for use.

Cylinder and Valve Description

Bromine trifluoride cylinders are equipped with an outlet designated as Compressed Gas Association (CGA) No. 670 which has a thread size of 1.030 inches and is left-hand with external threads. The mating connection seats on a flat washer.

CONNECTION 670 1.030"-14 LH EXT. using Face Washer

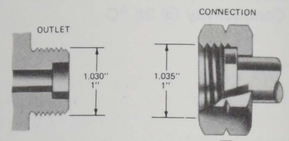


Fig. 1. CONNECTION 670 1.030"-14 RH EXT. using Face Washer.

Figure 1 illustrates the valve outlet and the mating connection used in this service.

Safety Devices

Since cylinders of bromine trifluoride are not equipped with safety devices, care should be taken to see that the cylinder is not overheated. Although bromine trifluoride is a high boiling liquid, excessive temperatures (over 51.7 °C (125 °F) may cause the liquid to expand, completely filling the cylinder, and create dangerous hydrostatic pressures.

Recommended Controls

Since bromine trifluoride is a liquid, its regulation from the cylinder can be effected by a manual needle valve. Matheson provides a Model 55A-670 monel needle valve for direct connection to a cylinder. This needle valve can be provided with ¼ inch compression fitting, ¼ inch male or female NPT. A serrated hose end is the usual outlet. A Model 60L monel needle valve is recommended for use with lecture bottles.

Shipping Regulations

Bromine trifluoride is shipped under DOT regulations in steel cylinders approved for shipment of compressed gases. It is shipped as a corrosive liquid, taking a "White Label".

Chemical Preparation

Bromine trifluoride is prepared by direct combination of 1 part bromine with 3 parts fluorine in a water-cooled copper reactor with temperature maintained in the range of 15–50 °C or by the reaction of BrF with F_2.

Chemical Properties

Bromine trifluoride is a powerful fluorinating agent. Metal chlorides, bromides and iodides are converted to fluorides by treatment with bromine trifluoride. Bromine trifluoride will react vigorously with water to give bromine, oxygen, and bromic and hydrofluoric acids.

Bromine trifluoride will convert many oxides to fluorides and oxyanions to fluoanions. Bromine trifluoride will react with sulfur, selenium, tellurium, phosphorus, arsenic, antimony, silicon and boron at room temperature or at slightly elevated temperatures to give the corresponding fluoride.

Ether, benzene and turpentine will burn immediately on contact with bromine trifluoride. Methyl chloride reacts upon contact with explosive violence. Carbon tetrachloride is relatively inert to bromine trifluoride at ambient temperatures but can be fluorinated and brominated at higher temperatures.

Thermodynamic and Detailed Physical Data

Molecular Structure (2)

The bromine trifluoride molecule has a distorted-T structure, with C_{2v} symmetry and a symmetry number of two. It has one short (Br-F_2) 1.72 × 10^{-10} m (1.721 Å) and two long (Br-F_1 and Br-F_3) 1.810 × 10^{-10} m (1.810 Å) Br-F bonds. The F_1-Br-F_2 bond angle is 86.21°, and the F_3-Br-F_1 bond angle is 187.58°.

Infrared Spectrum (6)

See Figure 2 for the infrared spectrum of gaseous bromine trifluoride.

Density (3)

The liquid density between 10 and 125 °C corresponds to the following equation:

$$d = 3.623 - 0.002\,77\,T \qquad (T = °K)$$

Some density values calculated by this equation are shown below.

Temperature, °C	Density, kg/l
10	2.839
20	2.811
30	2.783
40	2.756
50	2.728
60	2.700
70	2.672

The vapor pressure of bromine trifluoride, between 38–155 °C is described by the following equation:

$$\log_{10} p = 7.748\,53 - \frac{1\,685.8}{(t + 220.57)}$$

p = mmHg
t = °C

Values calculated from the above formula are as follows:

Temperature, °C	Vapor Pressure kPa	mbar	mmHg
38.72	2.354	23.54	17.66
49.10	4.093	40.93	30.7
57.00	6.310	63.10	47.33

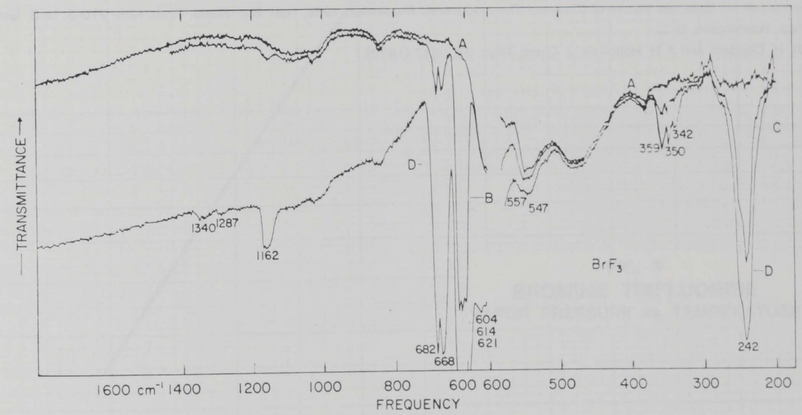


Fig. 2. Infrared spectrum of gaseous bromine trifluoride; 62 cm path length nickel cell, with AgCl windows: A, background; B, 0.0267 kPa (0.2 mmHg) pressure; C, 0.1333 kPa (1 mmHg) pressure; D, 0.7999 kPa (6 mmHg) pressure.

BROMINE TRIFLUORIDE

Temperature, °C	Vapor Pressure kPa	mbar	mmHg
66.23	9.897	98.97	74.23
76.36	15.73	157.3	118.0
84.94	22.67	226.7	170.05
91.84	30.00	300.0	225.05
101.75	43.98	439.8	329.9
111.85	63.41	634.1	475.6
121.96	89.50	895.0	671.3
125.75	101.325	1 013.25	760.0
126.84	104.94	1 049.4	787.1
131.86	123.04	1 230.4	922.9
137.30	145.47	1 454.7	1 091.1
148.30	210.01	2 010.1	1 507.7
154.82	241.34	2 413.4	1 810.2

See Figure 3 for vapor pressure curve.

Thermodynamic Properties of Bromine Trifluoride As Ideal Gas @ 25 °C

Heat Capacity, C_p°	66.496 J/(mol·°K) 15.897 cal/(mol·°C)
Entropy, S°	292.324 J/(mol·°K) 69.883 cal/(mol·°C)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/T$	−292.324 J/(mol·°K) −69.883 cal/(mol·°C)
Enthalpy Difference $H_0^\circ - H_{298}^\circ$	−14.276 kJ/mol −3.413 kcal/mol
Enthalpy of Formation, ΔH_f°	−255.588 kJ/mol −61.087 kcal/mol
Free Energy of Formation, ΔF_f°	−229.396 kJ/mol −54.827 kcal/mol
Molar Specific Heat, Liquid (4) @ 12.4 °C	124.06 J/(mol·°K) 29.651 cal/(mol·°C)
Entropy, Liquid @ 25 °C (5)	170.24 J/(mol·°K) 42.60 cal/(mol·°C)
Standard Heat of Formation, Liquid (5) @ 25 °C	−300.83 kJ/mol −71.90 kcal·mol
Free Energy of Formation, Liquid (5) @ 25 °C	−240.58 kJ/mol −57.50 kcal/mol

REFERENCES

[1] For an extensive tabulation of the thermodynamic and physical properties of bromine trifluoride, see W. Braker and A. L. Mossman, *The Matheson unabridged Gas Data Book, 1974*, Matheson, East Rutherford, New Jersey.

[2] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[3] O. Ruff and A. Braida, *J. Allgem. Anorg. Chem. 206*, 63 (1932).

[4] G. D. Oliver and J. W. Grisard, *J. Amer. Chem. Soc. 74*, 2705 (1952).

[5] D. D. Wagman, *et al.*, *Selected Values of Chemical Thermodynamic Properties, 1968*, Natl. Bur. Stand. Tech. Note 270-3, U. S. Government Printing Office, Washington, D. C.

[6] H. Selig, H. H. Claasen, and J. H. Holloway, *J. Chem. Phys. 52*, 3517 (1970).

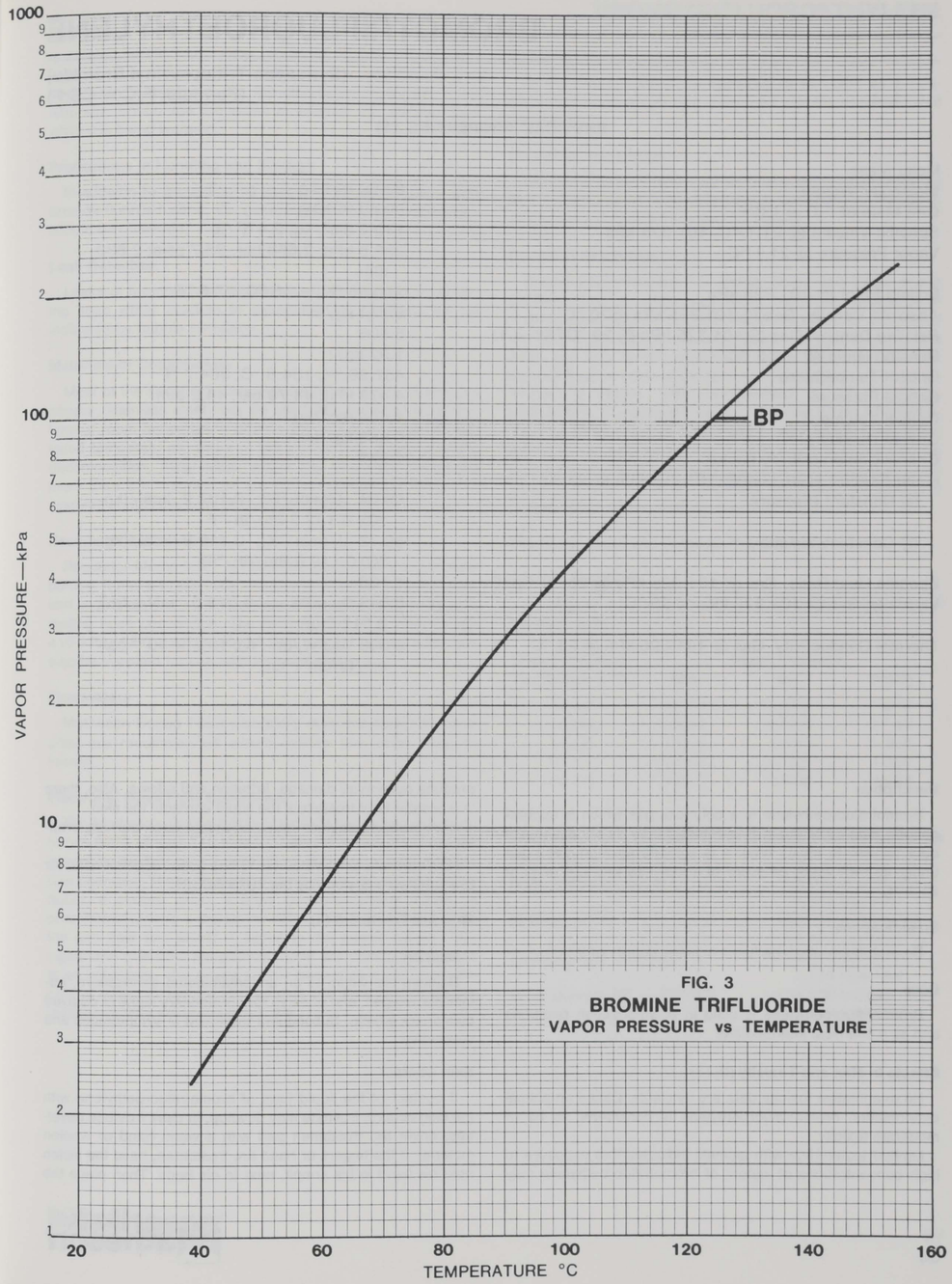


FIG. 3
BROMINE TRIFLUORIDE
VAPOR PRESSURE vs TEMPERATURE

BROMOTRIFLUOROETHYLENE

(Synonym: Trifluorovinyl Bromide)
(Formula: $F_2C = CBrF$)

VAPOR PRESSURE—kPa

PHYSICAL PROPERTIES (1)

Molar Mass	0.160 921 kg
Molecular Weight	0.160 921 kg
One Mole of $F_2C = CBrF$	149.8 dm^3/kg; 2.4 ft^3/lb
Specific Volume @ 21.1 °C, 101.325 kPa	266.8 kPa; 2.668 bar; 38.7 psia; 2.633 atm
Vapor Pressure @ 21.1 °C	270.65 °K; −2.5 °C; 27.5 °F
Boiling Point @ 101.325 kPa	6.754 kg/m^3
Absolute Density, Gas @ 101.325 kPa @20 °C	5.606
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	1.92 kg/l
Density, liquid @ −2.5 °C	457.99 °K; 184.8 °C; 364.7 °F
Critical Temperature	4 479 kPa; 44.79 bar; 44.2 atm
Critical Pressure	1.464 dm^3/kg
Critical Volume	0.683 kg/dm^3
Critical Density	0.277
Critical Compressibility Factor	
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	89.04 J/(mol·°K); 0.132 2 kcal/(kg·°C); 0.132 2 Btu/lb·°F
@ Constant Volume	80.73 J/(mol·°K); 0.119 9 kcal/(kg·°C) 0.119 9 Btu/(lb·°F)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C Cp/Cv	1.103
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.013 0 mPa·s; 0.013 0 mN·s/m^2; 0.013 0 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.008 033 W/(m·°K); 19.2 × 10^{-6} cal·cm/(s·cm^2·°C)

Description

Bromotrifluoroethylene is a colorless gas which is spontaneously flammable in air. It is detectable by its phosgene-like odor (similar to musty hay). It is shipped as a liquefied gas under its own vapor pressure of about 165 kPa (24 psig) at 21.1 °C.

Specifications

Bromotrifluoroethylene has a minimum purity of 97.0%.

Uses

Bromotrifluoroethylene is used in polymerization reactions and as a chemical intermediate.

Effects In Man and Toxicity (2) (3)

No quantitative toxicity data are available. Based on animal experiments, bromotrifluoroethylene is considered to be of moderate toxicity.

Limited experience with animals indicates that exposure to high concentrations of vapors of bromotrifluoroethylene may produce pulmonary damage, irritation and edema. Also, there is a possibility of frostbite if the liquid contacts the skin.

Bromotrifluoroethylene has inadequate odor warning properties.

No Threshold Limit Value (TLV) has been recommended for bromotrifluoroethylene by the 1979 ACGIH.

First Aid Treatment (4)

Inhalation

Remove the victim to an uncontaminated atmosphere, administer oxygen, and observe for premonitary signs of delayed pulmonary edema. Subsequent treatment is symptomatic and supportive.

Skin Contact

If contact of the liquid form of bromotrifluoroethylene with the skin occurs, frostbite may develop. In case frostbite develops, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation reestablish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

In addition to grounding all lines and equipment used with bromotrifluoroethylene, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks of bromotrifluoroethylene may be detected by applying soap water solution to suspected points; leaks will be indicated by bubble formation.

Materials of Construction

Most of the commonly used metals (steel, brass, aluminum, copper, stainless steel) may be used with bromotrifluoroethylene at room temperature provided the system is dry. At elevated temperatures, some of the metals may cause catalytic decomposition. Magnesium alloys and aluminum containing more than 2% magnesium are not recommended for use in systems containing bromotrifluoroethylene.

Recommended Controls

Regulator Model 3321 is recommended for use with lecture bottles. It has a brass body, neoprene diaphragm, Kel-F seat, and an angle style ⅛" NPT male outlet needle valve 112A with mating hose connection. The delivery pressure range is 28-410 kPa (4-60 psig). A Model 31B manual needle valve can also be supplied for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units are recommended where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ±1.2%

Shipping Regulations

Bromotrifluoroethylene is classified by the DOT as a flammable compressed gas and is shipped with the required "Red Gas Label".

Chemical Preparation

Bromotrifluoroethylene may be prepared by debromination of 1,1,2-tribromo-1,2,2-trifluorethane with zinc, or by dehydrobromination of $CBrF_2CHBrF$ by a base.

Chemical Properties

Bromotrifluoroethylene has olefinic properties. Vapor phase photobromination yields CBr_2FCBrF_2, but photochemical chlorination gives only 60% $CCl_2FCBrClF$ and 40% of scrambled bromo and chloro products. Bromotrifluoroethylene reacts with S_2Cl_2 and SCl_2 to give sulfides. It reacts with butyllithium or methyllithium in ether or pentane solution to give trifluorovinyllithium. It reacts with diethylamine to give $(C_2H_5)_2NCF_2CHBrF$. It undergoes the Grignard reaction in tetrahydrofuran as solvent to give $F_2C{:}CFMgBr$, from which many interesting compounds containing the trifluorovinyl group may be derived. It may be polymerized or telomerized to oils and resins covering a wide range of viscosities and having exceptionally high densities while retaining chemical stability.

Thermodynamic and Detailed Physical Data

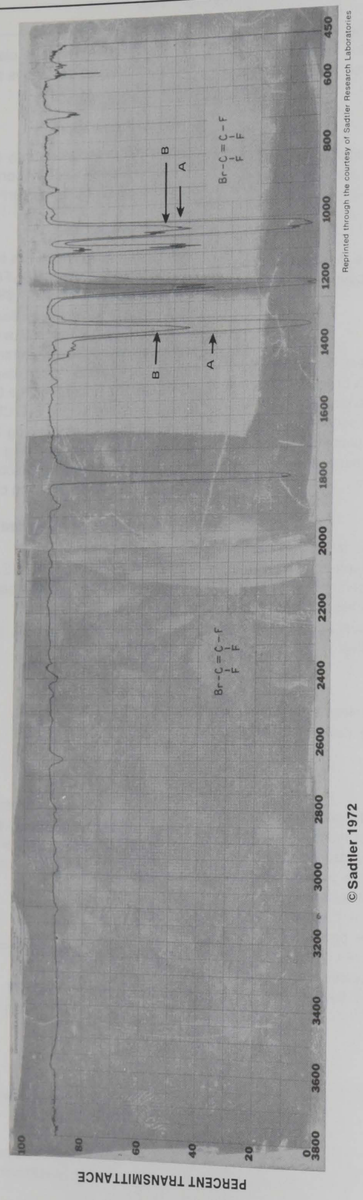
Infrared Spectrum

See Figure 1 for the infrared spectrum of gaseous bromotrifluoroethylene.

Vapor Pressure Temperature, °C	Vapor Pressure kPa	Vapor Pressure bar	Vapor Pressure mmHg
4.44	127.7	1.277	958
10.00	152.0	1.520	1 140
15.56	182.4	1.824	1 368
21.11	212.8	2.128	1 900
37.78	324.2	3.242	2 432

Thermodynamic Functions for Bromotrifluoroethylene as Ideal Gas @ 26.85 °C (5)

Heat Capacity, C_p°/R	43.300 J/(mol·°K)
	10.349 cal/(mol·°C)
Entropy, S°/R	168.582 J/(mol·°K)
	40.292 cal/(mol·°C)
Enthalpy, $(H_T^\circ - E_0^\circ)/RT$	30.016 kJ/mol
	7.174 kcal/mol
Free Energy, $(F_T^\circ - E_0^\circ)/RT$	−138.566 kJ/mol
	−33.118 kcal/mol



©Sadtler 1972

Fig. 1. Infrared spectrum of gaseous bromotrifluoroethylene; 10 cm path length cell, with KBr windows; cell pressure: curve A: 2.0 kPa (15 mmHg), curve B: 0.40 kPa (3 mmHg) (6).

REFERENCES

[1] For extensive tabulation of the thermodynamic and physical properties of bromotrifluoroethylene, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1974*, Matheson, East Rutherford, New Jersey.

[2] F. W. Patty, *Industrial Hygiene and Toxicology*, 2nd edition, *1962*, p. 1328, John Wiley & Sons, Inc., New York, New York.

[3] *Toxic Substances, 1974*, pp. 351, 477, HEW Publication No. (NIOSH) 74–134, National Institute for Occupational Safety and Health, Rockville, Maryland.

[4] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 103–105, Matheson, Lyndhurst, New Jersey.

[5] D. E. Mann, N. Acquista, and E. K. Plyler, *J. Chem. Phys. 22*, 1199–1202 (1954).

[6] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

BROMOTRIFLUOROMETHANE

(Synonyms: Trifluoromethyl Bromide; Freon-13B1®)
(Formula: $CBrF_3$)

PHYSICAL PROPERTIES (1)

Molar Mass	0.148 910 kg
Molecular Weight	0.148 910 kg
One Mole of $CBrF_3$	162.3 dm^3/kg; 2.6 ft^3/lb
Specific Volume @ 21.1 °C, 101.325 kPa	1 411.3 kPa; 14.11 bar; 207.7 psia; 13.93 atm
Vapor Pressure @ 21.1 °C	215.35 °K; −57.8 °C; −72.0 °F
Boiling Point @ 101.325 kPa	105.15 °K; −168.0 °C; −270.4 °F
Melting Point	6.291 kg/m^3
Absolute Density, Gas @ 101.325 kPa @ 25 °C	5.31
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.992 kg/l
Density, Liquid @ −57.8 °C	340.15 °K; 67.0 °C; 152.6 °F
Critical Temperature	3 964 kPa; 39.64 bar; 574.9 psia; 39.12 atm
Critical Pressure	1.343 dm^3/kg
Critical Volume	0.745 kg/dm^3
Critical Density	0.280
Critical Compressibility Factor	
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	70.590 kJ/(kmol·°K); 70.590 J/(mol·°K); 16.871 cal/(mol·°C); 0.113 Btu/(lb·°F)
@ Constant Volume	62.267 kJ/(kmol·°K); 62.267 J/(mol·°K); 14.882 cal/(mol·°C) 0.099 94 Btu/(lb·°F)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.134
Specific Heat, Liquid @ 0 °C	123.362 J/(mol·°K)
Viscocity, Gas @ 101.325 kPa @ 25 °C	0.0016 mPa·s; 0.0016 mN·s/m^2; 0.0016 cP
Viscocity, Liquid @ −40 °C	0.32 mPa·s; 0.32 mN·s/m^2; 0.32 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.002 09 W/(m·°K); 20.9 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −40 °C	0.022 2 W/(m·°K); 222 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −40 °C	13.0 mN/m; 13.0 dyn/cm
Solubility In Water @ 101.325 kPa @ 25 °C	0.03% (by weight)
Refractive Index, Liquid, n_D @ 25 °C	1.238
Relative Dielectric Strength, (Nitrogen = 1)	1.83

Description

Bromotrifluoroethylene is a colorless, nonflammable, non-corrosive gas. It is shipped as a liquefied gas under its own vapor pressure of 1 310 kPa (190 psig) at 21.1 °C.

Specifications

Bromotrifluoromethane has a minimum purity of 99.0 mole %, the remainder being traces of other Freons and air.

Uses

Apart from its possible use as a chemical intermediate, bromotrifluoromethane finds uses as a fire extinguishing agent.

Effects in Man and Toxicity (2)

Inhalation of high concentrations of gas can cause such symptoms as dizziness, disorientation, incoordination, narcosis, nausea, or vomiting. There appear to be no irreversible

Matheson

effects once the oxygen deficiency has been corrected. Skin contact with liquid bromotrifluoromethane can cause skin irritation or frostbite. Bromotrifluoromethane is relatively nontoxic.

First Aid Treatment (2)

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration (if needed) and oxygen simultaneously. Treat symptomatically thereafter.

Skin Contact

In case of skin contact with the low boiling liquid, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frost bitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Leak Detection

Leaks of bromotrifluoromethane may be detected by applying soap water solution to suspected points; leaks will be indicated by bubble formation. Leaks of bromotrifluoromethane in dark, confined or inaccessible spaces or locations may be located by means of a halide torch or lamp. The Matheson Gas Leak Detector Model 8016 and 8017 provides a more sensitive method for detecting leaks.

Disposal of Leaking Cylinders

Leaking cylinders of bromotrifluoromethane may be disposed of according to the procedure outlined in Appendix II-C for inert gases.

Cylinder and Valve Description

Bromotrifluoromethane is shipped in DOT approved, steel cylinders. Cylinders containing bromotrifluoromethane are equipped with brass valves with Compressed Gas Association (CGA) outlet connection No. 320, the approved standard connection. The valve outlet has a thread size of 0.825 inch with right-hand external threads with a flat seat and requires a washer (see Figure 1). Lecture bottles have a special 9/16 inch-18 threads per inch male and 5/16 inch-32 threads per inch female dual outlet.

Materials of Construction

Most of the commonly used metals (steel, brass, aluminum, copper, stainless steel) may be used satisfactorily with bromotrifluoromethane under normal conditions of use.

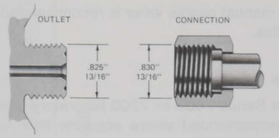


Fig. 1. CONNECTION 320 .825"-14 RH EXT. used with Flat Seat and Washer.

Washers made from Kel-F or from vulcanized fiber showed no swelling or other adverse effects when immersed in liquid bromotrifluoromethane for 2 weeks.

Piping and vessels to contain bromotrifluoromethane should be adequately designed to withstand the pressures to be encountered.

Safety Devices

Cylinders containing bromotrifluoromethane are equipped with frangible discs as safety devices. Cylinders should, therefore, be stored away from sources of heat to avoid developing pressures capable of rupturing the disc.

Recommended Controls

Automatic Pressure Regulators

Single stage regulator Model 1P-320 is recommended for use with bromotrifluoromethane. The regulator has a brass body, neoprene diaphragm, neoprene seat, and a Model 100S outlet needle valve with ¼" NPT male threads on the outlet with mating hose end connection. The delivery pressure range of this regulator is 28-240 kPa (4-35 psig). No cylinder pressure gauge is necessary since it will not indicate cylinder content but only vapor pressure which will remain constant as long as any liquid remains in the cylinder. Cylinder content is determined by weight. To prevent suckback of foreign materials a check valve is recommended for use with the regulator.

Automatic regulator Model 1L-320 can also be used with bromotrifluoromethane. It is similar in construction to the Model 1P-320 regulator, but differs in having a cylinder pressure gauge and a delivery pressure range of 28–550 kPa (4–80 psig).

Regulator Model 70-320 is recommended when accurate low pressure control is desired. The delivery pressure range of this regulator is 3.4–34.5 kPa (0.5–5 psig).

Regulator Model 3321 is recommended for use with lecture bottles.

Manual Controls

Matheson needle valve Model 50-320, a brass bar stock valve, is available for direct attachment to the cylinder valve outlet. The valve may be equipped with a variety of outlets, such as serrated hose end, ¼" compression fitting, male or female NPT pipe. It should be used only where supervised flow control is available and should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged, or if the system itself is closed. A

Matheson

BROMOTRIFLUOROMETHANE

Model 31B manual needle valve is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 or 7200 laboratory brass flowmeter units are recommended where accurate flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes. Flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Bromotrifluoromethane is classified by the DOT as a nonflammable compressed gas and is shipped with the required "Green Label".

Commercial Preparations

Bromotrifluoromethane is prepared by the thermal bromination of fluoroform in a nonmetallic reactor at 400–600 °C, and by brominolysis of perfluoropropane at 700–1 000 ° C in a nonmetallic reactor where the products are bromotrifluoromethane, bromopentafluoroethane and dibromodifluoromethane, which are then separated by fractional distillation.

Chemical Properties

Bromotrifluoromethane is thermally stable. Anhydrous $CBrF_3$ or $CBrF_3$ with 3% (by volume) of water is not corrosive to steel, brass, or aluminum after exposure at 120 °C (248 °F) for 260 days. Copper and stainless steel show no detectable corrosion upon immersion for 7 days in bromotrifluoromethane containing 3 volume % water. Hydrolysis of bromotrifluoromethane containing water solution in the presence of brass test pieces on storage at 60 °C shows 0.062 kg bromotrifluoromethane per liter of solution was hydrolyzed after 720 hours; with iron test pieces under similar conditions, hydrolysis proceeds to the extent of 0.070 kg per liter of solution after 300 hours. Due to the significant difference in reactivity between the bromine and fluorine atoms it may be possible to use bromotrifluoromethane as a chemical intermediate.

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

Bromotrifluoromethane has C_{3v} symmetry, a symmetry number of three with C—F and C—Br bond distances of 1.328×10^{-10} m (1.328 Å) and 1.909×10^{-10} m (1.909 Å), respectively, and F—C—F and F—C—Br bond angles of 108.6° and 110.33°, respectively.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous bromotrifluoromethane.

Vapor Pressure (4)

The vapor pressure of liquid bromotrifluoromethane in the temperature range of 156.15–218.15 °K is represented by the following equation:

$$\log_{10} p = 16.075 - \frac{1\,250.75}{T} - 3.165\,1 \log_{10} T$$

in which p = mmHg and T = °K

Some vapor pressure values calculated by the equation are shown below.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
156.15	1.77	17.7	13.3
163.15	3.40	34.0	25.5
173.15	7.80	78.0	58.5
183.15	16.20	162.0	121.5
193.15	30.88	308.8	231.6
203.15	54.85	548.5	411.4
213.15	91.58	915.8	686.9
215.35	101.36	1 013.6	760.3
218.15	116.04	1.160.4	870.4

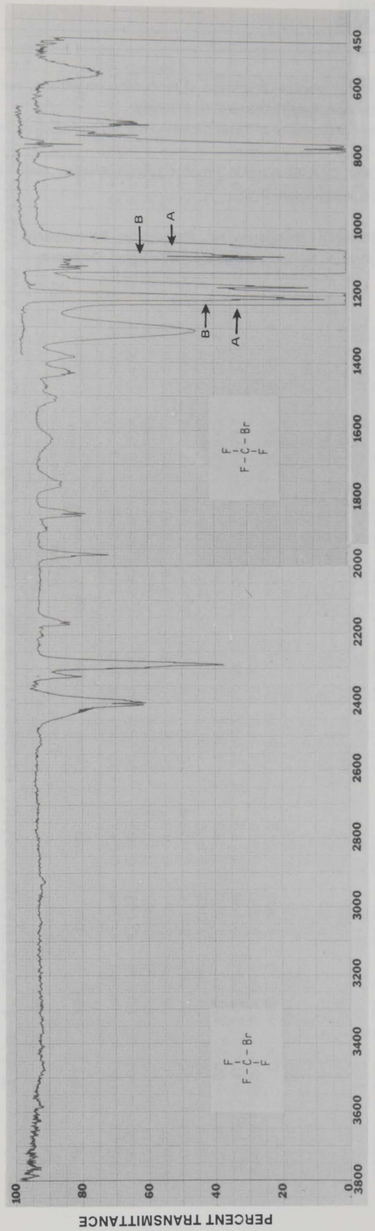
For additional vapor pressure data, see Table 1 and Figure 3.

Thermodynamic Data

Thermodynamic properties of the saturated liquid and vapor and of the superheated vapor are listed in Tables 1 and 2, respectively.

Thermodynamic Properties of Bromotrifluoromethane As Ideal Gas @ 25 °C (3)

Heat Capacity, C_p°	69.329 J/(mol·°K)
	16.570 cal/(mol·°C)
Entropy, S°	297.713 J/(mol·°K)
	71.155 cal/(mol·°C)
Free Energy Function, $\{F_{298}^\circ - H_{298}^\circ)/T$	−297.713 J/(mol·°K)
	−71.155 cal/(mol·°C)
Enthalpy Difference, $H_O^\circ - H_{298}^\circ$	14.468 kJ/mol
	3.458 kcal/mol
Enthalpy of Formation, ΔH_f°	−648.938 kJ/mol
	−155.100 kcal/mol
Free Energy of Formation, ΔF_f°	−622.659 kJ/mol
	−148.819 kcal/mol



© Sadtler 1972

Reprinted through the courtesy of Sadtler Research Laboratories

Fig. 2. Infrared spectrum of gaseous bromotrifluoromethane in the frequency range 3 800-450 cm^{-1}; 10 cm path length cell, with KBr windows; curve A obtained at a cell pressure of 2.666 kPa (20 mmHg), curve B at 0.066 7 kPa (0.5 mmHg) (5).

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of bromotrifluoromethane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, 1974, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, 1977, pp. 119-123, Matheson, Lyndhurst, New Jersey.

[3] *JANAF Thermochemical Tables*, 2nd edition, 1971, D. A. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser; Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[4] A. A. Banks, *et al., J. Chem. Soc. 1948*, 2188.

[5] *The Sadtler Standard Spectra*, 1972, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[6] *Freon-13B1*, Tech. Bull. T-13b1, 1963, E. I. duPont de Nemours & Co., Inc., Wilmington, Delaware.

Matheson®

Matheson®

Table 1. THERMODYNAMIC PROPERTIES OF THE SATURATED LIQUID AND VAPOR (6)

Temperature		Pressure			Entropy J/(mol•°K)		Enthalpy kJ/mol		Latent Heat of Vaporization kJ/mol	Specific Volume dm^3/kg		Density kg/dm^3	
°K	°F	kPa	bar	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
166.48	−160	4.399	0.044	0.043 4	−32.149	86.540	−6.407	13.361	19.768	0.456 35	2 106.82	2.191 3	0.000 475
177.59	−140	10.694	0.107	0.105 5	−26.292	82.490	−5.393	13.921	19.314	0.465 71	922.00	2.147 3	0.001 09
188.71	−120	23.056	0.231	0.227 5	−20.685	79.251	−4.365	14.493	18.858	0.475 08	452.02	2.104 9	0.002 21
199.82	−100	45.103	0.451	0.445 1	15.264	76.758	−3.316	15.071	18.387	0.485 69	242.81	2.058 9	0.004 12
210.93	−80	81.427	0.814	0.803 6	10.031	74.765	−2.243	15.645	17.888	0.496 93	140.43	2.012 4	0.007 12
215.37	−72	101.224	1.012	0.999	7.975	74.079	−1.803	15.877	17.680	0.501 92	114.81	1.992 3	0.008 71
222.04	−60	137.55	1.376	1.358	−4.984	73.207	−1.139	16.220	17.359	0.509 41	86.25	1.963 1	0.011 6
233.15	−40	219.804	2.198	2.169	0.000	71.961	0.000	16.777	16.777	0.523 15	55.63	1.911 5	0.018 0
244.26	−20	334.946	3.350	3.306	4.860	70.964	1.170	17.317	16.147	0.538 13	37.33	1.858 3	0.026 8
255.37	0	490.629	4.906	4.842	9.657	70.154	2.378	17.829	15.451	0.554 99	25.864	1.801 8	0.038 7
266.48	20	694.99	6.95	6.86	14.330	69.469	3.624	18.303	14.679	0.574 34	18.379	1.741 1	0.054 4
277.59	40	955.61	9.55	9.43	19.003	68.784	4.912	18.729	13.817	0.596 81	13.310	1.675 6	0.075 1
288.71	60	1 282.42	12.83	12.66	23.675	68.098	6.258	19.089	12.831	0.623 03	9.770	1.605 1	0.102 4
299.82	80	1 685.07	16.85	16.63	28.286	67.288	7.667	19.356	11.689	0.655 49	7.217	1.525 6	0.138 6
310.93	100	2 173.22	21.73	21.45	33.083	66.291	9.179	19.494	10.315	0.697 95	5.319	1.423 8	0.188 0
322.04	120	2 760.65	27.61	27.25	38.192	64.796	10.862	19.425	8.563	0.759 12	3.858	1.317 3	0.259 2
333.15	140	3 459.78	34.60	34.15	44.236	62.242	12.911	18.920	6.009	0.872 12	2.647	1.146 6	0.377 8
338.71	150	3 855.53	38.55	38.05	48.659	59.625	14.458	18.175	3.717	1.028 19	2.023	0.972 6	0.494 3
340.15 (critical)	152.6	3 963.78	39.64	39.12						1.342 20	1.342 20	0.745 0	0.745 0

Table 2. THERMODYNAMIC PROPERTIES OF THE SUPERHEATED VAPOR (6)

H, ENTHALPY, kJ/mol; **S**, ENTROPY, J/(mol·°K); **V**, SPECIFIC VOLUME, dm^3/kg

Pressure kPa	bar	atm		Temperature, °K 199.82	227.59	255.37	283.15	310.93	338.71	366.48	394.26	422.04	449.82	477.59	505.37
			H	15.112	16.732	18.456	20.280	22.197	24.202						
20.670	0.207	0.204	S	83.363	90.901	98.066	104.858	111.275	117.505						
			V	534.8	610.7	686.3	761.7	837.1	912.4						
			H	15.088	16.711	18.438	20.266	22.187	24.191	26.278					
34.451	0.345	0.340	S	79.001	86.602	93.767	100.559	107.038	113.206	119.125					
			V	319.1	365.0	410.6	456.1	501.5	546.8	592.0					
			H		16.659	18.397	20.228	22.152	24.164	26.250					
68.901	0.689	0.680	S		80.746	87.911	94.702	101.182	107.412	113.331					
			V		180.7	203.8	226.8	249.7	272.5	295.3					
			H		16.611	18.355	20.193	22.125	24.136	26.230					
101.325	0.103 25	1.000	S		77.381	84.609	91.462	97.942	104.172	110.091					
			V		121.7	137.7	153.6	169.3	184.9	200.5					
			H		16.556	18.310	20.155	22.090	24.108	26.202	28.369				
137.903	1.379	1.361	S		74.702	81.930	88.783	95.325	101.555	107.474	113.440				
			V		88.46	100.4	112.2	123.8	135.4	146.9	158.4				
			H			18.130	20.006	21.962	23.994	26.102	28.279				
275.807	2.758	2.722	S			75.699	82.677	89.282	95.512	101.493	107.225				
			V			48.63	54.82	60.87	66.85	72.76	78.63				
			H			17.940	19.847	21.827	23.880	26.001	28.189	30.435			
413.710	4.137	4.083	S			71.836	78.939	85.606	91.961	97.942	103.674	109.219			
			V			31.32	35.67	39.87	43.98	48.03	52.03	55.99			
			H				19.685	21.689	23.762	25.898	28.096	30.356			
551.579	5.516	5.444	S				76.135	82.927	89.282	95.387	101.119	106.664			
			V							35.66	38.718	41.746			
			H				19.511	21.547	23.641	25.794	28.006	30.273			
689.473	6.895	6.805	S				73.892	80.746	87.163	93.331	99.126	104.671			
			V							28.23	30.74	33.20			
			H				19.034	21.169	23.326	25.524	27.770	30.065	32.408		
1 034.21	10.342	10.207	S				69.344	76.509	83.176	89.406	95.325	100.932	106.291		
			V							18.32	20.08	21.81	23.49		
			H					20.751	22.990	25.243	27.531	29.854	32.221		
1 378.95	13.789	13.609	S					73.145	80.061	86.478	92.459	98.191	103.611		
			V							13.35	14.76	16.11	17.42		
			H					20.273	22.630	24.953	27.282	29.643	32.035		
1 723.68	17.236	17.011	S					70.154	77.444	83.986	90.154	95.948	101.431		
			V							10.36	11.56	12.69	13.78		
			H					19.698	22.239	24.645	27.029	29.425	31.844	34.288	
2 068.42	20.684	20.414	S					67.226	75.076	81.867	88.160	94.017	99.562	104.858	
			V							8.36	9.41	10.41	11.35	12.27	
			H						21.803	24.319	26.766	29.203	31.650	34.122	
2 413.16	24.132	23.816	S						72.771	79.936	86.353	92.334	97.942	103.300	
			V							6.92	7.88	8.77	9.61	10.43	
			H						21.311	23.977	26.493	28.975	31.457	33.952	
2 757.893	25.579	27.218	S						70.528	78.067	84.733	90.777	96.509	101.867	
			V						4.75	5.82	6.73	7.55	8.32	9.05	

Matheson®

Matheson®

Table 2—*Continued*

Pressure kPa	bar	atm		Temperature, °K 199.82	227.59	255.37	283.15	310.93	338.71	366.48	394.26	422.04	449.82	477.59	505.37
			H						20.726	23.611	26.213	28.746	31.263	33.779	
3 102.630	31.027	30.621	S						68.161	76.322	83.176	89.406	95.200	100.621	
			V						3.87	4.97	5.83	6.59	7.30	7.98	
			H						19.972	23.212	25.922	28.511	31.062	33.609	
3 447.367	34.474	34.023	S						65.419	74.640	81.743	88.098	93.954	99.437	
			V						3.10	4.27	5.11	5.83	6.49	7.12	
			H						18.691	22.782	25.621	28.272	30.865	33.436	36.012
3 792.103	37.921	37.425	S						61.182	72.896	80.372	86.852	92.771	98.378	103.611
			V						2.26	3.69	4.51	5.21	5.83	6.42	6.97
			H							22.308	25.306	28.026	30.660	33.267	35.859
4 136.840	41.368	40.827	S							71.089	79.001	85.668	91.711	97.319	102.615
			V							3.20	4.02	4.69	5.28	5.83	6.36

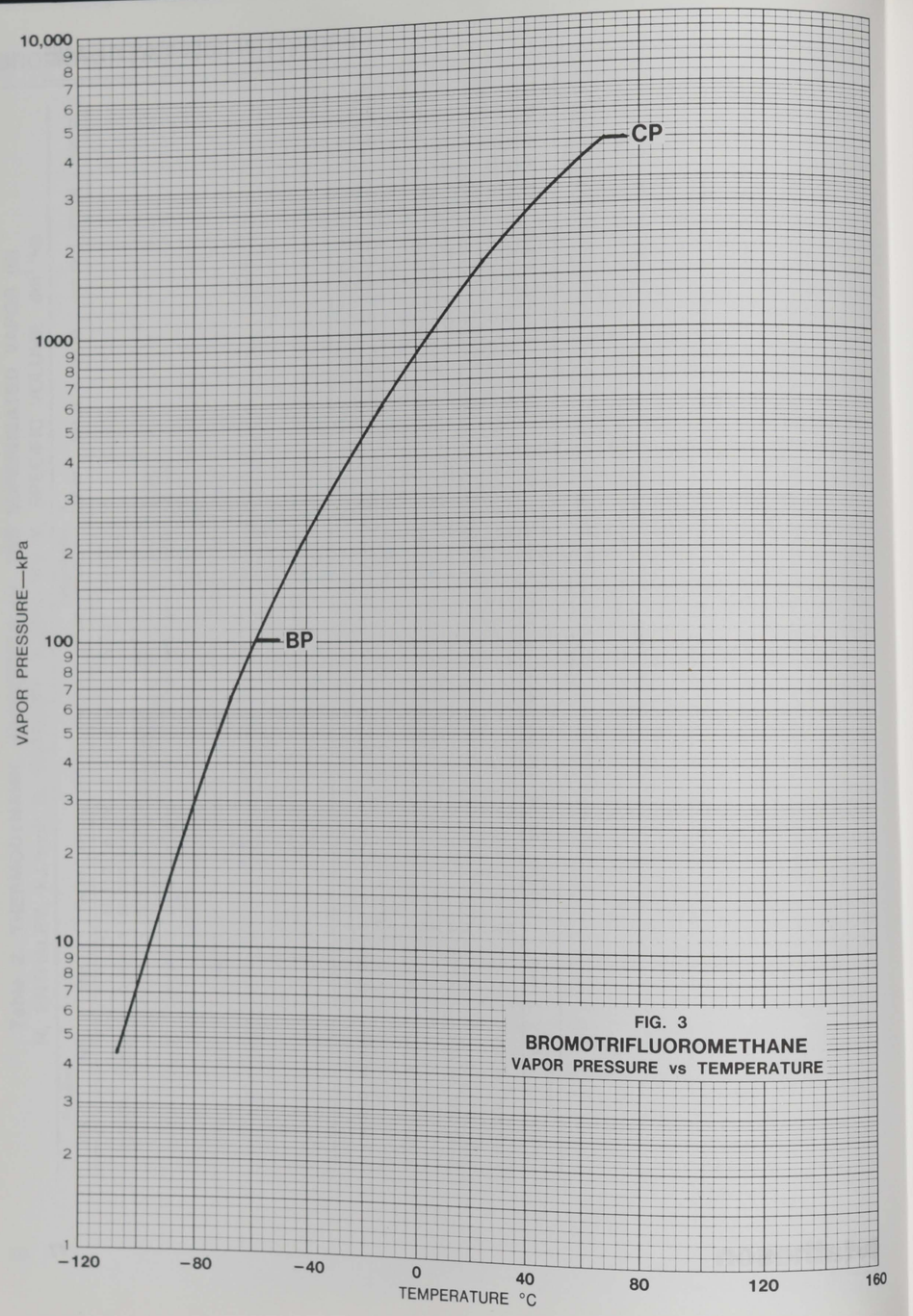


FIG. 3
BROMOTRIFLUOROMETHANE
VAPOR PRESSURE vs TEMPERATURE

1,3-BUTADIENE

(Synonyms: Biethylene, Erythrene; Vinylethylene)
(Formula: $H_2C:CHCH:CH_2$ or C_4H_6)

PHYSICAL PROPERTIES (1)

Molar Mass	0.054 092 kg
Molecular Weight	0.054 092 kg
One Mole of C_4H_6	430.6 dm^3/kg; 6.9 ft^3/lb
Specific Volume @ 21.1 °C, 101.325 kPa	248.9 kPa; 2.49 bar; 36.1 psia; 2.46 atm
Vapor Pressure @ 21.1 °C	
Boiling Point @ 101.325 kPa	268.74 °K; −4.4 °C; 24.1 °F
Melting Point @ 101.325 kPa	164.25 °K; −108.9 °C; −164.0 °F
Absolute Density, Gas @ 101.325 kPa @ 0 °C	2.428 kg/m^3
Relative Density, Gas @ 101.325 kPa @ O °C (Air = 1)	1.878
Density, Liquid @ Saturation Pressure @ 20 °C	0.621 kg/l
Critical Temperature	425.15 °K; 152.0 °C; 305.6 °F
Critical Pressure	4 327 kPa; 43.27 bar; 627.5 psia; 42.7 atm
Critical Volume	4.086 dm^3/kg
Critical Density	0.245 kg/dm^3
Critical Compressibility Factor	0.270
Latent Heat of Fusion @ −108.9 °C	147.624 kJ/kg; 7 985.3 kJ/mol; 35.283 kcal·kg
Flammability Limits in Air	2.0–11.5% (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	82.132 kJ/(kmol·°K); 82.132 J/(mol·°K); 0.363 kcal/(kg·°K)
@ Constant Volume	73.803 kJ/(kmol·°K) 73.803 J/(mol·°K) 0.326 kcal/(kg·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C Cp/Cv	1.113
Molar Specific Heat, Liquid @ −28.2 °C	111.169 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.007 54 mPa·s; 0.007 54 $mN·s/m^2$; 0.007 54 cP
Viscosity, Liquid @ −40 °C	0.33 mPa·s; 0.33 $mN·s/m^2$; 0.33 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.015 69 W/(m·°K); 37.5 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −40 °C	0.154 8 W/(m·°K); 370.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −40 °C	20.7 mN/m; 20.7 dyn/cm
Solubility in Water @ 101.325 kPa @ 27.3 °C	0.05% (by weight)
Autoignition Temperature	690.95 °K; 417.8 °C; 784.0 °F
Refractive Index, Liquid, n_D @ −25 °C	1.429 2
Heat of Combustion, Gas @ 25 °C and Constant Pressure	
Gross, to form H_2O(liq) + CO_2(gas)	2 541.74 kJ/mol; 607.49 kcal/mol
Net, to form H_2O(gas) + CO_2(gas)	2 409.69 kJ/mol; 575.93 kcal/mol
Heat of Combustion, Liquid @ 25 °C and Constant Pressure	
Gross, to form H_2O(liq) + CO_2(gas)	252.32 kJ/mol; 602.37 kcal/mol
Net, to form H_2O(gas) + CO_2(gas)	2 388.31 kJ/mol; 570.82 kcal/mol

Description

1,3-Butadiene is a colorless, flammable gas at room temperature and atmospheric pressure. The gas has a mildly aromatic odor. Butadiene is slightly soluble in methanol and ethanol and readily soluble in ether, benzene, carbon tetrachloride, and chloroform. Butadiene is a noncorrosive material. It is normally shipped as a liquefied gas under its own vapor pressure in steel cylinders or in insulated tank cars. Because of its extreme reactivity and tendency to polymerize, this material is shipped with an inhibitor. The cylinder pressure is 150 kPa (21.4 psig) at 21.1 °C.

Specifications

Matheson supplies three grades of 1,3-butadiene having specifications as follows:

1. Research Grade

This grade has the highest possible purity, typically 99.86 mole %.

2. Instrument Grade

This grade has a minimum purity of 99.5 mole %.

3. C.P. Grade

This grade has a minimum purity of 99.0 mole %. The C.P. Grade is similar to a grade referred to as Rubber Grade.

All grades contain approximately 115 ppm tertiary-butycatechol as a polymerization inhibitor. The inhibitor may be removed by distillation or by washing with dilute caustic soda solution.

Uses

1,3-Butadiene has been widely used in the manufacture of synthetic rubber. It has been extensively used in various polymerizations in the plastic industry and is particularly useful in the Diels-Alder reaction where it combines with activated olefins to give hydroaromatic compounds. 1,3-Butadiene is useful in a variety of miscellaneous reactions, which are described in the section on Chemical Properties.

Butadiene is finding increasing usage in the resins and plastics fields. Copolymers containing a high percentage of styrene have been widely used as reinforcing and stiffening resins for rubber, as water and solvent-based paints, and in combinations with polystyrene for high impact plastics. Mixtures of styrene-acrylonitrile resins and butadiene-acrylonitrile rubbers have produced exceptionally high impact plastics having good chemical and heat distortion properties.

Effects In Man (2)

1,3-Butadiene has some degree of anesthetic action and is mildly irritating to the mucous membranes and/or acts as a simple asphyxiant. Thus, depending on the concentration and time of exposure, symptoms such as rapid respiration, air hunger, diminished mental alertness, muscular incoordination, faulty judgment, emotional instability, rapid fatigue, nausea, vomiting, prostration and loss of consciousness, convulsions, and finally deep coma and death may occur.

Contact of the liquid form of the hydrocarbon with the skin can cause frostbite. Symptoms of frostbite are the change of skin from pink to white or grayish-yellow, pain which quickly subsides, and a cold and numb feeling.

Toxicity (2)

1,3-Butadiene has a low order of inhalation toxicity. Its vapors are mildly irritating to the mucous membranes. Some of the aliphatic hydrocarbons are detectable by odor in low concentrations, generally above 0.5%; e.g., methane has a sweet, oil type odor. However, the odors of this group of compounds do not provide adequate warning of hazardous concentrations.

The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 1000 ppm (2200 mg/m^3) for 1,3-butadiene.

First Aid Treatment (2)

Inhalation

The conscious person who becomes aware of any of the above mentioned symptoms should go promptly to an uncontaminated area and inhale fresh air or oxygen. However, in the event of massive exposure the victim may become unconscious or symptoms of asphyxiation may persist. In that case, the person should be removed promptly to an uncontaminated atmosphere and given artificial respiration and then oxygen, after breathing has been restored. Treat symptomatically thereafter.

Skin Contact

If contact of the liquid form of 1,3-butadiene with the skin occurs, frostbite may develop. In case frostbite develops, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The hazards associated with the handling and storage of butadiene arise from its high flammability and its extreme chemical reactivity. Butadiene should be stored upright in a cool, dry, well-ventilated location away from sources of heat, open flames, and sparks. Reserve stocks of this material should be segregated from cylinders containing oxygen, other oxidizing chemicals and gases, and combustible materials. Because of the tendency of butadiene to dimerize, the material should be kept as cool as possible. The following table gives the effect of temperature on the rate of formation of dimer.

Temperature, °F	% Butadiene Dimerized Per Hour
68	0.000 15
104	0.001 4
140	0.013
176	0.12
212	1.1

The dimer, 1-vinyl-3-cyclohexene, is miscible with butadiene in all proportions at ordinary temperatures. The dimer does not tend to undergo further polymerization to any major extent. No inhibitor for the dimerization reaction is known at the present time. However, to minimize the formation of dimer the butadiene should be stored at as low a temperature as possible.

On contact with air butadiene readily forms peroxides. This peroxide formation can be prevented by excluding air, or by the use of inhibitors such as tertiary-butycatechol. This inhibitor will protect only the liquid butadiene in which it is dissolved. Once the butadiene has been freed from the inhibitor by distillation or by caustic scrubbing, exposure to air will cause peroxides to form. The peroxide content will have a definite effect on the rate of polymer formation. Any polymers forming due to peroxide content will not be soluble in the butadiene, and they may separate out and be troublesome in many operations. In order to minimize this peroxide formation, the temperature should be maintained at a minimum, and contact with oxygen or air should be avoided.

Cylinders should never be refilled except by the supplier.

All indoor storage areas should be provided with continuous ventilation. Since this gas is heavier than air and tends to seek lower levels, storage pits and depressions in basements should be avoided.

Butadiene fires are difficult and dangerous to extinguish. Therefore, it is advisable to try and control the fire by shutting off the source of the fuel, and by keeping all adjacent areas and objects wetted with water spray. Small fires may be extinguished with carbon dioxide or dry chemical fire extinguishers. For further information see *Properties and Essential Information for Safe Handling and Use of Butadiene*, Pamphlet SD-55, the Chemical Manufacturing Assn., 1825 Connecticut Ave., N.W., Washington, D. C. 20009.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Areas suspected of leaks should be painted with a soap solution; leaks will be evident by the formation of small bubbles. Under no circumstances should a match or flame be used to detect butadiene leaks.

Disposal of Leaking Cylinders

Leaking cylinders of 1,3-butadiene may be disposed of by the procedure listed in Appendix II-A.

Materials of Construction

Since butadiene is considered a noncorrosive material, it may be used with any common or commercially available material. Piping systems or vessels to contain butadiene should be designed to have a working pressure as specified by competent engineers and using a safety factor conforming to the A.M.S.E. code for pressure piping.

Cylinder and Valve Description

Butadiene is shipped in DOT approved cylinders. The cylinder valve used by Matheson and most other butadiene suppliers is a diaphragm type packless valve having a Compressed Gas Association (CGA) valve outlet No. 510. The outlet specifications are 0.885 inch diameter, internal left-hand threads accepting a bullet-shaped nipple, as is shown in Figure 1. This

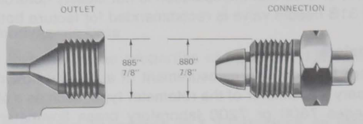


Fig. 1. CONNECTION 510 .885"-14 LH INT. accepting a Bullet Shaped Nipple

valve is normally used in liquefied petroleum gas service. Lecture bottles have a special 9/16 inch-18 threads per inch male and 5/16"-32 threads per inch female outlet.

Safety Devices

Safety devices required on butadiene cylinders depend to some extent on the type of cylinder in which the material is contained. A 73.9 °C (165 °F) fusible metal alloy is permitted; however, when cylinders are over 30 inches long, exclusive of the neck, this device is required at both ends. A frangible disc is allowed on cylinders having a minimum required test pressure of 20 680 kPa (3 000 psig) or higher. The most commonly used safety device, and that used by Matheson, is a safety relief valve or what is commonly known as a spring-loaded "pop" valve. With this type of safety device, the safety relief valve is usually incorporated in the cylinder valve, and only one of this type of device is required in any cylinder. When the cylinder pressure exceeds a preset value [about 2 590 kPa (375 psig)] usually due to excessive heat, the relief valve will open and relieve the pressure until it returns below the preset relief pressure of the device.

Recommended Controls

Automatic Pressure Regulator

Matheson supplies single stage regulator Model 1P-510 for use with butadiene. The regulator has a brass body with brass internal parts, fabric-reinforced neoprene rubber diaphragm, and neoprene seat. It has a delivery pressure range of 28–240 kPa (4–35 psig). No tank gauge is supplied with the regulator since the vapor pressure of gaseous butadiene over liquid butadiene will remain constant as long as any liquid remains in the cylinder; therefore, the pressure is no indication of cylinder content, which must be determined by weighing.

For sensitive and accurate low pressure regulation, Matheson supplies a Model 70 regulator. The regulator has an oversize, pancake body of die cast aluminum and a Buna N diaphragm, rubber seat and brass needle valve outlet, 1/4" NPT male, and hose connection. The delivery pressure range of this regulator is 3.4–34.5 kPa (0.5–5.0 psig).

Regulator Model 3321 with a delivery pressure range of 28–410 kPa (4–60 psig) is available for use with lecture bottles.

Manual Controls

Manual needle valve Model 50-510, a brass bar stock valve, is available for direct connection to the cylinder valve outlet.

This valve is ideal for intermittent supervised flow control, but it should not be used to control pressure since unsafe pressures may build up in a closed system if a relief device is not included, or if careful manipulation is not closely controlled. A Model 31B needle valve is recommended for lecture bottles.

Flowmeters

Where the accurate measurement of a definite flow rate is necessary a flowmeter of the rotameter type, such as a Matheson Series 7600 or 7200 laboratory brass flowmeter unit, should be utilized.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes. Flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

1,3-Butadiene is classified by the DOT as a flammable compressed gas, and therefore requires a "Red Gas Label". Butadiene is approved for shipment only if it contains an inhibitor.

Preparations

Most of 1,3-butadiene available commercially is produced by catalytic dehydrogenation of n-butane and 1- and 2-butenes, or by thermal cracking of petroleum distillates (naphtha and light gas oils). It can also be obtained by simultaneous dehydrogenation and dehydration of ethyl alcohol by metallic oxides; by the reaction of a mixture of ethyl alcohol and acetaldehyde over silica gel containing a little tantalum oxide; by converting acetaldehyde to aldol, followed by hydrogenation and dehydration; by reacting acetylene with formaldehyde, hydrogenating the resulting 2-butyne-1,4-diol and dehydrating the reduction product (1,4-butanediol).

Chemical Properties of 1,3-Butadiene

1. It is a precursor in the manufacture of synthetic rubbers.
2. Being a conjugated diene, it forms adducts with a wide variety of dienophiles (Diels-Alder reaction).
3. It undergoes dimerization to 4-vinylcyclohexene on heating at elevated temperatures under pressure in the presence of silicon carbide or copper or chromium nephtenates as catalysts. In the presence of nickel catalysts, cyclodimerization occurs, leading to 1,5-cyclooctadiene. In the presence of titanium or chromyl halides and aluminum alkyls, trimerization occurs, giving 1,5,9-cyclododecatriene. 1,3-Butadiene is readily polymerized, giving polybutadiene by 1,4-addition and by 1,2-addition.
4. 1,3-Butadiene undergoes 1,4-cyclization with reactants containing sulfur, oxygen, and nitrogen. Thus, with sulfur (at elevated temperatures) it gives thiophene in 6% yield, while with hydrogen sulfide, (in the presence of catalysts) it gives thiophene in 30–50% yield. It reacts practically quantitatively with sulfur dioxide to give 3-sulfolene. With ammonia, at elevated temperatures and in the presence of catalysts, it forms pyrrole in 6% yield. It reacts with diazomethane in ether solution at −20 °C to form 5-vinylpyrazoline and 5,5′-dipyrazoline. It reacts with dimethylaniline at 350 °C over zinc oxide-silica gel in the presence of steam to form quinoline and its homologs in 70% yield. the acid-catalyzed reaction of 1,3-butadiene and formaldehyde gives a variety of products, including 4-vinyl-1,3-dioxane and a cyclic formal. 1,3-Butadiene reacts with substances containing the cyano group. Thus, it reacts with cyanogen at 480 °C to give 2-cyanopyridine in 18% yield. Hydrogen cyanide reacts with 1,3-butadiene at 50–150 °C in the presence of nickel carbonyl or cuprous chloride to form 1-cyan-2-butene. Passage of 1,3-butadiene through a solution of thiocyanogen in ether gives 1,4-dithiocyano-2-butene in 80% yield.
5. 1,3-Butadiene reacts with chlorine, bromine, iodine, hydrogen chloride, hydrogen bromide, hydrogen iodine, hypochlorus acid, etc. by 1,2- and/or 1,4-mechanisms, depending on the reactant and reaction conditions.

Thermodynamic and Detailed Physical Data

Molecular Structure

The chemical behavior of 1,3-butadiene can be explained by the resonance theory, the molecule being considered as a resonance hybrid of the structures

$$CH_2{:}CHCH{:}CH_2 \leftrightarrow CH_2{:}CHCH{:}CH_2 \leftrightarrow \overset{+}{\underline{C}}H_2{:}CHCH{:}\overline{C}H_2$$

$$\leftrightarrow \overline{C}H_2{:}CHCH{:}\overline{C}H_2$$

with a resonance energy of 14.644 kJ/mol. The butadiene molecule has a planar conformation with a transoid orientation, the more stable and predominant conformation at room temperature, or a cisoid orientation which is required by stereochemical considerations in some of its reactions. Bond lengths are: C—H = 1.05 Å, C—C = 1.35 Å. In 1,3-butadiene the electrons are delocalized and are spread over the entire conjugated system.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous 1,3-butadiene.

Vapor Pressure (3)

The vapor pressure of 1,3-butadiene between −66 and 146 °C is represented by the following equation:

$$\log_{10} p = A - \frac{B}{t + c}$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.859 41, 935.53 and 239, respectively.

Some vapor pressure values calculated by this equation are shown below.

Temperature, °C	Vapor Pressure kPa	mbar	mmHg	atm
−66	3.92	39.2	29.4	0.039
−40	19.77	197.7	148.3	0.195
−20	52.88	528.8	396.6	0.522
−4.4	101.325	1 013.25	760.0	1.000
0	119.82	1 198.2	898.7	1.183
20	238.51	2 385.1	1 789.0	2.354
40	434.36	4 343.6	3 258.0	4.287
46	554.75	5 547.5	4 161.0	5.475

Other vapor pressure data are shown in Table 1 and Figure 3.

Latent Heat of Vaporization, ΔHv (4)

Temperature, °C	ΔHV, kJ/kg
−26.1	436.06
−4.6	416.06
22.5	388.09

Thermodynamic Data

For thermodynamic properties of saturated 1,3-butadiene, see Table 1.

Thermodynamic Properties of 1,3-Butadiene as Ideal Gas @ 25 °C

Heat Capacity, C_p°	79.538 J/(mol·°K) 19.010 cal/(mol·°C)
Entropy, S°	278.738 J/(mol·°K) 66.620 cal/(mol·°C)
Enthalpy Difference, $(H_{298}^\circ - H_{273}^\circ)$	1 911.67 J/mol 456.9 cal·mol
Enthalpy of Formation, ΔH_f°	110.165 kJ/mol 26.33 kcal/mol
Free Energy of Formation, ΔF_f°	150.666 kJ/mol 36.01 kcal/mol

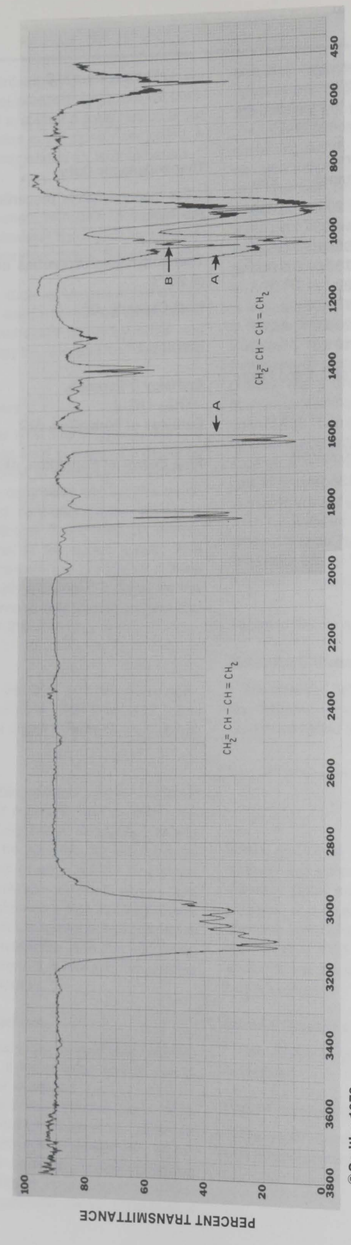


Fig. 2. Infrared spectrum of 1,3-butadiene; 10 cm path length cell, with KBr windows; curve A obtained at a cell pressure of 0.345 kPa (50 mmHg), curve B (partial scan) at 0.669 kPa (10 mmHg) (5).

Matheson

REFERENCES

[1] For extensive tabulations of thermodynamic and physical properties of 1,3-butadiene, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1974*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 11–16, Matheson, Lyndhurst, New Jersey.

[3] **Selected Values of Properties of Hydrocarbons and Related Compounds**, American Petroleum Institute, Research Project 44, Carnegie Press, Carnegie Institute of Technology, Pittsburgh, Pennsylvania (now at Texas A & M University, College Station, Texas).

[4] R. B. Scott, *et al.*, *J. Research Natl. Bur. Stand* 35, 39 (1945).

[5] **The Sadtler Standard Spectra,** *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[6] C. H. Meyers, C. S. Cragoe, and E. F. Mueller, *J. Research Natl. Bur. Stand. 39*, 507 (1947).

Matheson

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED 1,3-BUTADIENE (6)

Temperature		Pressure			Entropy J/(mol·°K)		Enthalpy kJ/mol		Latent Heat of Vaporization kJ/mol	Specific Volume dm^3/kg		Density kg/dm^3	
°K	°F	kPa	bar	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
166.48	−160	0.090	0.000 9	0.000 89	135.181	300.011	15.641	43.089	27.448	1.313 5	281 176	0.761 3	0.000 004
177.59	−140	0.310	0.003 1	0.003 06	141.835	293.153	16.785	43.667	26.882	1.333 5	87 774	0.749 9	0.000 011
188.71	−120	0.896	0.009 0	0.008 85	148.150	287.586	17.942	44.258	26.316	1.354 7	32 244	0.738 2	0.000 031
199.82	−100	2.268	0.022 7	0.022 39	154.125	283.105	19.099	44.874	25.775	1.376 5	13 528	0.726 5	0.000 074
210.93	−80	5.102	0.051 0	0.050 35	159.828	279.506	20.281	45.516	25.235	1.399 6	6 333	0.714 5	0.000 158
222.04	−60	7.419	0.074 2	0.073 2	165.305	276.632	21.463	46.182	24.719	1.423 4	3 246	0.702 5	0.000 308
233.15	−40	19.767	0.197 7	0.195 1	170.601	274.369	22.670	46.861	24.191	1.448 3	1 795	0.690 5	0.000 557
244.26	−20	34.943	0.349 5	0.344 9	175.716	272.604	23.889	47.552	23.663	1.474 5	1 058	0.678 2	0.000 945
255.37	0	58.336	0.583 3	0.575 7	180.695	271.246	25.134	48.269	23.135	1.502 0	657.1	0.665 8	0.001 52
266.48	20	92.734	0.927 3	0.915 2	185.561	270.272	26.417	48.986	22.569	1.531 4	427.0	0.653 0	0.002 34
277.59	40	141.273	1.412	1.394	190.336	269.548	27.712	49.702	21.990	1.562 6	288.2	0.640 0	0.003 47
288.71	60	207.600	2.076	2.049	195.021	269.096	29.044	50.432	21.388	1.596 3	200.9	0.626 4	0.004 98
299.82	80	295.370	2.954	2.915	199.638	268.824	30.415	51.148	20.733	1.631 9	143.9	0.612 8	0.006 95
310.93	100	408.858	4.088	4.035	204.209	268.688	31.811	51.865	20.054	1.671 8	105.4	0.598 2	0.009 49
322.04	120	552.34	5.52	5.45	208.736	268.711	33.269	52.582	19.313	1.714 9	78.78	0.583 1	0.012 69
333.15	140	730.36	7.31	7.21	213.240	268.801	34.753	53.261	18.508	1.762 3	59.78	0.567 4	0.016 73
344.26	160	947.34	9.47	9.35	217.721	268.937	36.287	53.927	17.640	1.816 0	45.96	0.550 7	0.021 76
355.37	180	1209.3	12.10	11.94	222.179	269.118	37.884	54.556	16.672	1.877 2	35.68	0.532 7	0.028 03
366.48	200	1520.3	15.20	15.00	226.547	269.322	39.606	55.197	15.591	1.948 4	27.87	0.513 2	0.035 88

Matheson®

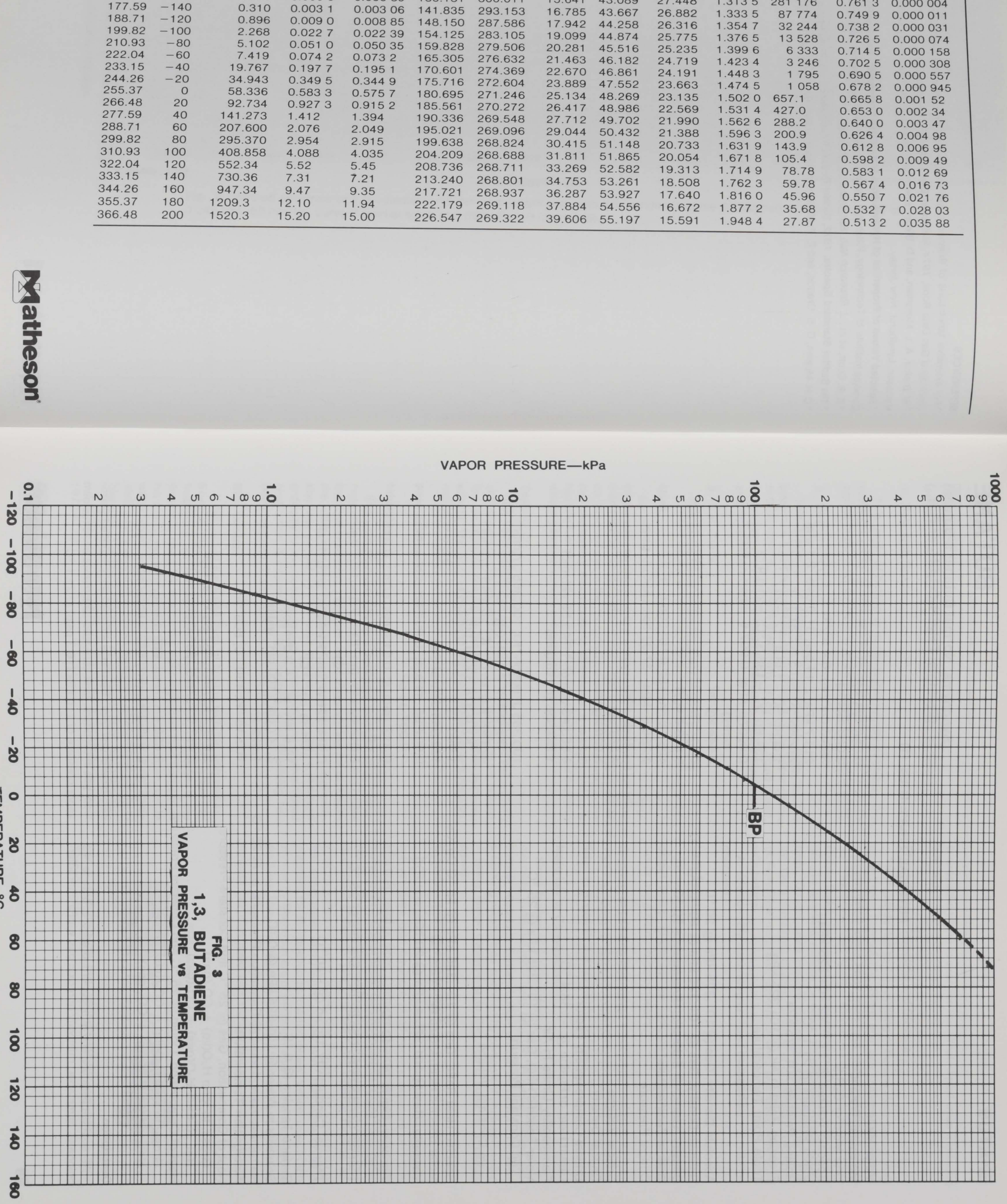


FIG. 3
1,3, BUTADIENE
VAPOR PRESSURE vs TEMPERATURE

BUTANE

(Synonyms: Normal Butane; n-Butane)
(Formula: $CH_3CH_2CH_2CH_2$ or C_4H_{10})

PHYSICAL PROPERTIES (1)

Molar Mass	0.058 124 kg
Molecular Weight	0.058 124 kg
One Mole of C_4H_{10}	399.5 dm^3/kg; 6.4 ft^3/lb
Specific Volume @ 21.1 °C, 101.325 kPa	213.7 kPa; 2.14 bar; 31.0 psia; 2.1 atm
Vapor Pressure @ 21.1 °C	272.65 °K; −0.5 °C; 31.1 °F
Boiling Point @ 101.325 kPa	134.80 °K; −138.4 °C; −217.0 °F
Freezing Point in Air @ 101.325 kPa	134.86 °K; −138.3 °C; −216.9 °F
Triple Point Temperature	0.00076 kPa; 0.007 6 mbar; 0.005 7 mmHg
Pressure	
Absolute Density, Gas @ 101.325 kPa @ 20 °C	2.544 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	2.11
Density, Liquid @ Saturation Pressure @ 20 °C	0.578 8 kg/l
Critical Temperature	425.16 °K; 152.0 °C; 305.6 °F
Critical Pressure	3 796.6 kPa; 37.97 bar; 550.7 psia; 37.47 atm
Critical Volume	4.387 dm^3/kg
Critical Density	0.228 kg/dm^3
Critical Compressibility Factor	0.274
Latent Heat of Fusion @ −138.4 °C	4 663.43 J/mol; 1 145.59 cal/mol
Flammability Limits In Air	1.8–8.4% (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	100.365 J/(kmol·°K); 100.365 J/(mol·°K); 0.412 7 kcal/(kg·°C)
@ Constant Volume	92.048 kJ/(kmol·°K); 92.048 J/(mol·°K); 0.378 5 kcal/(kg·°C)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C Cp/Cv	1.090
Molar Specific Heat, Liquid @ −42.4 °C	122.544 J/(mol·°K)
Viscosity, Gas @ 101.325 4 kPa @ 20 °C	0.007 35 mPa·s; 0.007 35 mN·s/m^2; 0.007 35 cP
Viscosity, Liquid @ −40 °C	0.313 mPa·s; 0.313 mN·s/m^2; 0.313 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.014 644 W/(m·°K); 35.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −40 °C	0.014 226 W/(m·°K); 340.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 0 °C	14.8 mN/m; 14.8 dyn/cm
Solubility in Water @ 101.325 kPa @ 0 °C	3.147 cm^3/100 cm^3 water
Refractive Index, Liquid @ Saturation Pressure, n_D @ 25 °C	1.329 2
Autoignition Temperature	703.15 °K; 430 °C; 806 °F
Heat of Combustion, Gas @ 25 °C and Constant Pressure	
Gross, to form H_2O(liq) + CO_2(gas)	2 877.1 kJ/mol; 687.64 kcal/mol
Net, to form H_2O(gas) + CO_2(gas)	2 657.0 kJ/mol; 635.0 kcal.mol
Heat of Combustion, Liquid @ 25 °C and Constant Pressure	
Gross, to form H_2O(liq) + CO_2(gas)	2 855.4 kJ/mol; 682.4 kcal/mol
Net, to form H_2O(gas) + CO_2(gas)	2 635.3 kJ/mol; 629.9 kcal/mol

Description

At room temperature and atmospheric pressure, butane is a colorless, flammable, relatively nontoxic gas with a characteristic natural gas odor. Butane is shipped as a liquefied petroleum gas in cylinders, tank cars, and tank trucks under its own vapor pressure of 110 kPa (16.3 psig) at 21.1 °C.

Matheson

Specifications

Matheson supplies three grades of butane, as follows:

1. Research Grade

This grade of butane is of the highest purity available. The minimum purity of this grade is 99.9 mole %, although its typical purity is 99.99 mole % as determined by freezing point.

2. Instrument Grade

This grade has a minimum purity of 99.5 mole %. The maximum non-condensable or air content of the vapor phase is 0.05 mole %. There is essentially no air in the liquid phase. Special precautions are taken to eliminate traces of water, oil, and nonvolatile matter.

3. C.P. Grade

This grade has a minimum purity of 99.0 weight %.

Uses

Butane in pure form is used for calibration work in instruments such as pressure and temperature gauges and for filling thermobulbs for such instruments. It is industrially important as an intermediate in the manufacture of aviation fuel and in the manufacture of many organic chemicals. It is also used as a heating fuel and a special motor fuel, usually in in-plant trucking where gasoline vapors are considered obnoxious.

Toxicity (2)

The 1979 ACGIH has adopted a Threshold Limit Value (TLV) of 600 ppm (1430 mg/m^3) for butane.* Exposure to 1% butane for ten minutes results in drowsiness but no other systemic effects. The odor of butane is not detectable below a concentration of 0.5%.

First Aid Treatment (2)

Inhalation

The conscious person who becomes aware of any drowsiness should go promptly to an uncontaminated area and inhale fresh air or oxygen. However, in the event of massive exposure the victim may become unconscious or symptoms of asphyxiation may persist. In that case, the person should be removed promptly to an uncontaminated atmosphere and given artificial respiration if needed and then oxygen, after breathing has been restored. Treat symptomatically thereafter.

Skin Contact

If contact of the liquid form of butane with the skin occurs, frostbite may develop. In case frostbite develops, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit next to his body. Then place the frostbitten part in warm water, about 42°C (108 °F). If warm water is not available, or it is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

* Notice of Intended Change to 800 ppm (1900 mg/m^3), 1979 ACGIH.

Precautions in Handling and Storage

The hazards due to the handling of butane stem mainly from its extreme flammability. Store and use butane cylinders in well-ventilated areas away from heat and all ignition sources such as flames and sparks. Never use flames to detect flammable leaks, use soap water solution. Do not use butane around sparking motors or other nonexplosion-proof equipment. Do not store reserve stocks of butane cylinders with cylinders containing oxygen, chlorine or other highly oxidizing or flammable materials. Ground all lines and equipment used with butane.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

All fittings and joints should be painted with soap solution to detect leaks, which will be indicated by bubble formation. Never use a flame to detect leaks.

Disposal of Leaking Cylinders

For disposal of leaking cylinders of butane the procedure listed in Appendix II-A should be followed.

Materials of Construction

Since butane is a noncorrosive gas, any common or commercially available metal may be used. However, piping systems or vessels to contain butane should be designed to have a working pressure as specified by competent engineers using a safety factor conforming to the ASME code for pressure piping.

Cylinders and Valve Description

DOT approved cylinders containing butane are usually of the low pressure type having a rated service pressure of 1 030 kPa (150 psig) or more. Cylinders of butane are equipped with valves having Compressed Gas Association (CGA) valve outlet No. 510 (for gas withdrawal) having a thread size of 0.885 inch diameter-14 threads per inch left-hand internal threads accepting a bullet-shaped nipple. See Figure 1 for illustration of the valve outlet and mating connection. This valve outlet is standard for all liquefied petroleum gases. Valves used in this service by Matheson are of the diaphragm type and contain no packing. They are therefore relatively leak-free and require no packing adjustments. Lecture bottles have a special 9/16"-18 threads per inch male and 5/16"-32 threads per inch female valve outlet.

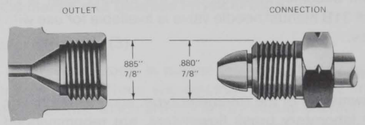


Fig. 1. CONNECTION 510 .885"-14 LH INT. accepting a Bullet Shaped Nipple

Matheson

Safety Devices

A number of different safety devices are permitted on cylinders containing butane. A frangible disc is allowed in cylinders having a minimum required test pressure of 20 680 kPa (3 000 psig) or higher, and is required in only one end of the container. A 73.9 °C (165 °F) fusible metal may be used; however, when cylinders are over 30 inches long (exclusive of the neck) this device is required in both ends. A frangible disc backed up with 73.9 °C (165 °F) fusible metal is permitted in cylinders having a minimum required test pressure of 20 680 kPa (3 000 psig) or higher and when cylinders are over 30 inches long (exclusive of the neck) this device is required at both ends. The most commonly used safety device, which is employed by Matheson, is the spring-loaded safety relief valve. If cylinder pressure becomes dangerously high, usually due to overheating, the safety relief device will open (at approximately 2 590 kPa (375 psig)) and release butane gas until the pressure again returns to a safe level.

Recommended Controls

Automatic Pressure Regulators

Single stage automatic regulator Model 1P-510 is recommended for butane service. This regulator has a brass body, with brass internal parts, fabric-reinforced Neoprene rubber diaphragm, and Neoprene seat. It has a delivery pressure range of 28–240 kPa (4–35 psig). It has a delivery pressure gauge, but no tank gauge, since tank pressure is no criterion of the amount of gas remaining; tank pressure will remain constant as long as liquid butane remains in the cylinder.

For low pressure regulation, Matheson supplies a Model 70 regulator. The regulator has an oversized pancake body of die cast aluminum with a Buna N diaphragm. The regulator gives sensitive and very accurate low pressure control. The delivery pressure range of this regulator is 3.4–45 kPa (0.5–5 psig).

This regulator is designed primarily for liquefied petroleum gases where it is particularly suited for fuel gas burner operation, since it delivers a steady flow for a stable flame. It is ideal for use with flame photometers.

Regulator Model 3321 with a delivery pressure range of 28–410 kPa (4–60 psig) is available for use with lecture bottles.

Manual Controls

Manual needle valve Model 50-510, a brass bar stock valve, is available for direct connection to the cylinder valve outlet. The valve may be equipped with a variety of outlets such as ¼" compression fitting, ¼" NPT male or female pipe, or serrated hose end. It should be used only where supervised flow control is available and should not be used as a pressure control since it will not prevent pressures from building up if a system becomes clogged or if the system itself is closed. A Model 31B manual needle valve is available for use with lecture bottles.

Flowmeters

Flowmeters of the rotameter type, such as Matheson Series 7600 laboratory brass flowmeters, are recommended where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes. Flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Butane is classified by the DOT as a flammable, compressed gas and is shipped with the required "Red Gas Label".

Commercial Preparation

Butane and isobutane are recovered from natural and refinery gases. Recovery from natural gas is effected by absorption at high pressures in a suitable absorber oil and subsequent fractionation to remove propane and the pentanes. The two butanes are then separated by careful fractionation. Recovery of the butanes from refinery gases is effected by compression and condensation, but the recent trend has been toward the use of the absorption methods used with natural gas.

Chemical Properties

Butane is a member of the alkane or paraffin series of hydrocarbons. The alkanes as a group are chemically inert substances, not being attacked by cold bromine, sulfuric acid, and nitric acid. However, the alkanes undergo (with a change in conditions) both chlorination and nitration and, in addition, many thermal reactions such as isomerization, dehydrogenation, cyclization, and others. When the alkanes are heated from 500 °C upwards, they undergo complex reactions which may be accelerated or directed by different catalysts to give a variety of products. The following reactions exemplify the different types of reactions which the alkanes undergo and which are of great importance to the petroleum industry. The reactions which may occur simultaneously are: (a) dehydrogenation, (b) isomerization, (c) thermal degradation or cracking, (d) aromatization.

(a) Dehydrogenation

This reaction is of importance in the petroleum industry for the conversion of ethane, propane, butane, isobutane, and pentanes into olefins wherein higher yields and higher reaction velocities are promoted by catalysts. Industrially, the olefins so obtained are polymerized or used for alkylating isoalkanes to produce high grade motor fuel. Ethylene, propylene and isobutylene are used for the manufacture of a great variety of industrially important aliphatic compounds.

(b) Isomerization

Normal chain alkanes containing four or more carbon atoms, or slightly branched alkanes, undergo isomerization to more highly branched alkanes with catalysts of the Friedel-Crafts type at temperatures of 150–200 °C. The most effective catalyst is aluminum chloride supported on silica gel or alumina, and promoted by hydrogen chloride, but a wide variety of other catalysts and promoters may be used. Thus, isobutane and isopentane are produced from butane and pentane, respectively, and can be alkylated by propylene and the butylenes to yield highly branched heptanes, octanes and nonanes for use in aviation fuels.

(c) Thermal Degradation or Cracking

The pyrolysis of gaseous, liquid and solid alkanes at temperatures of about 500–1 000 °C has been widely studied with the object of obtaining lower branched chain alkanes and olefins. Non-catalytic pyrolysis of alkanes at about 1 400–1 600 °C results in more complete degradation to yield the industrially important carbon black, hydrogen and acetylene. By the use of suitable catalysts, the cracking temperature can be reduced to 200–500 °C and by careful control of the conditions, the desired products can be obtained in good yields.

(d) Aromatization

The alkanes can be converted into aromatic hydrocarbons by high temperature cracking and by hydroforming (or catalytic reforming). The aromatization of alkanes occurs at a temperature of 500–1 000 °C most likely by the mechanism of first forming olefins and diolefins which combine to yield cyclic compounds. The latter in the presence of metallic catalysts are dehydrogenated into aromatic compounds. In the hydroforming process, practically quantitative conversion is effected of aliphatic hydrocarbons containing more than six carbon atoms in the chain, to yield aromatic hydrocarbons with the same number of carbon atoms. The mechanism of this reaction involves dehydrogenation of the alkane into an olefin, cyclization of the olefin to a cyclohexane derivative, and dehydrogenation of the cyclic compound to an aromatic compound.

Other Reactions of Alkanes:

(e) Oxidation

Alkanes can be oxidized by atmospheric oxygen at temperatures well below their ignition point. The rate of oxidation of the alkanes in the vapor phase increases with the length of chain and decreases by the chain branching. Methyl groups have a stabilizing effect.

(f) Halogenation

The halogens (except iodine) react readily with alkanes. Little or no halogenation occurs in the dark, but in daylight or ultraviolet light methane and ethane are attacked (except by iodine) with explosive violence. Halogenation of the alkanes may be effected in the liquid or gaseous state with ultraviolet light or heat; catalysts may accelerate the reaction. The formation of isomeric halides and polysubstitution products and, with chlorine, the danger of explosive reaction may be minimized by control of concentrations, temperature and catalysts, and in the case of chlorination, by carrying out the reaction in the liquid phase with carbon dioxide, nitrogen, steam, hydrogen chloride or chlorinated hydrocarbons as diluents.

(g) Nitration

While alkanes show little or no reactivity towards nitric acid or nitrogen tetroxide at ordinary temperatures, reaction proceeds at temperatures of 100–450 °C in the liquid phase and preferably in the vapor phase to give nitroalkanes.

(h) With Inorganic Reagents

(1) Under ultraviolet light the alkanes react with a mixture of sulfur dioxide and chlorine at room temperature to give sulfonyl chlorides. (2) In the presence of organic peroxides, the alkanes react with sulfuryl chloride in the dark to yield alkyl chloride, sulfur dioxide, and hydrogen chloride. (3) Alkanes (e.g., propane, butane, and isobutane) react with sulfur dioxide in the vapor phase yielding sulfonic acids or their anhydrides, sulfones, and sulfates. (4) At about 300 °C and above, alkanes containing four or more carbon atoms react with sulfur to give olefins, diolefins and thiophene derivatives. (5) Alkanes, including propane, 3-methylpentane and heptane, react with phosphorus trichloride and oxygen at 25 °C to yield alkanephosphonyl chlorides which, on hydrolysis, give alkylphosphonic acids. (6) In the presence of aluminum chloride, alkanes react with carbon monoxide to give ketones (e.g., isobutanes yield methyl isopropyl ketone).

(i) With Organic Reagents

(1) In the presence of actinic light, or in the dark in the presence of organic peroxides, alkanes (e.g., pentane, heptane and isooctane) react with oxalyl chloride or phosgene to give acid chlorides. (2) Normal alkanes react with acid chlorides in the presence of aluminum chloride to give ketones. (3) Isoalkanes condense with haloalkanes in the presence of Friedel-Crafts catalysts, e.g., isobutane and vinyl chloride in the presence of aluminum chloride yield 1,1-dichloro-3,3-dimethylbutane. (4) Isoalkanes undergo halogen-hydrogen exchange with tertiary or secondary alkyl halides in the presence of aluminum halides. (5) Isoalkanes react with unsaturated aliphatic carboxylic acids in the presence of aluminum chloride to give saturated fatty acids. (6) Tertiary alkanes react with benzoyl peroxide yielding tert-alkyl benzoate, benzene and carbon dioxide or (if the reaction takes this course) tert-alkylbenzene, benzyl alcohol and carbon dioxide. (7) Tertiary alkanes and ketones in the presence of sulfuric acid react to give tert-alcohols. (8) Isoalkanes condense with aromatic hydrocarbons in the presence of silica or alumina.

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

The four carbon atoms in butane are linked to one another in a straight chain. Three two-electron single bonds link the four carbon atoms, which are formed by mutual sharing of two electrons between each of the carbon atoms. There are six two-electron carbon-to-hydrogen bonds on the two terminal

carbon atoms. These hydrogen atoms are equivalent, since only one monosubstitution product is formed by replacement of any one of these six hydrogen atoms. The four hydrogen atoms on the two interior carbon atoms are also equivalent but the environment is different from that of the six terminal hydrogen atoms. Thus, while only one monosubstitution product is formed by replacement of any of these hydrogen atoms, it is different, although isomeric, from the monosubstitution product formed by replacement of any one of the six terminal hydrogen atoms.

The butane molecule exists in eclipsed and staggered conformational isomers. Corresponding to eclipsed conformations are a syn form (cis form) with C_{2v} symmetry and two equivalent anti forms (gauche forms) with C_2 symmetry. The staggered anti conformation (C_{2h} symmetry) has a single trans form, but two equivalent syn forms with C_2 symmetry are possible. (See Figure 2 for conformations of butane.) Since the staggered conformations have the lowest potential energy, the molecule will mostly adopt one or more of the three staggered conformations, depending on the state of butane (solid, liquid, gas).

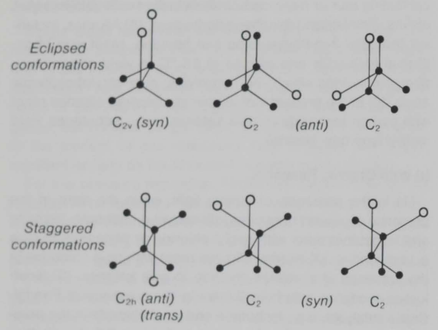


Fig. 2. Conformations of butane; blank circles represent methyl groups, large dark circles carbon atoms, and smaller dark circles hydrogen atoms (3).

Infrared Spectrum

See Figure 3 for the infrared spectrum of gaseous butane.

Vapor Pressure (4)

The vapor pressure of liquid butane between −60 and 45 °C is represented by the following Antoine vapor pressure equation:

$$\log_{10} p = A - \frac{B}{t + c}$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.830 29, 945.9, and 240.0, respectively.

Some vapor pressure values calculated by this equation are shown below:

Temperature, °C	Vapor Pressure kPa	bar	mmHg
−60	3.9	0.039	37.6
−40	16.5	0.165	126.1
−20	50.4	0.504	339.4
−0.5	101.325	1.013 25	760.0
20	207.6	2.076	1 557.0
30	283.0	2.830	2 123.0
45	430.0	4.300	3 225.0

For additional vapor pressure data, see Table 1 and Figure 4.

Latent Heat of Vaporization

@ −0.5 °C	22.393 kJ/mol
@ 25 °C	21.066 kJ/mol

Thermodynamic Data

Thermodynamic properties of saturated butane and superheated butane are listed in Table 1 and 2, respectively.

Thermodynamic Properties of Butane As Ideal Gas @ 25 °C

Heat Capacity, C_p^o	97.447 J/(mol°K)
Entropy, S^o (4)	310.034 J/(mol°K)
Enthalpy of Formation, ΔH_f^o	−126.148 kJ/mol
Free Energy of Formation, ΔF_f^o	−17.154 kJ/mol

REFERENCES

[1] For extensive tabulations of thermodynamic and physical properties of butane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, 1974, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, 1977, pp. 11–16, Matheson, Lyndhurst, New Jersey.

[3] M. Avram and G. D. Mateescu, *Infrared Spectroscopy*, 1972, pp. 127–128, John Wiley & Sons, Inc., New York, New York.

[4] F. D. Rossini, *et al.*, *Selected Values of Properties of Hydrocarbons and Related Compounds*, 1953, American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pennsylvania (now at Texas A & M University, College Station, Texas).

[5] *The Sadtler Standard Spectra*, 1972, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[6] W. R. Woolrich, *Handbook of Refrigerating Engineering*, 4th edition, 1965, Volume 1, pp. 236–237, the AVI Publishing Co., Inc., Westport, Connecticut.

[7] B. H. Sage, D. C. Webster, and W. N. Lacey, *Ind. Eng. Chem.* 29, 1188 (1937).

Reprinted through the courtesy of Sadtler Research Laboratories
©Sadtler 1972

Fig. 3. Infrared spectrum of gaseous butane; 10 cm path length cell. With KBr windows: curve A obtained at a cell pressure of 6.666 kPa (50 mmHg), curve B at 0.667 kPa (5 mmHg) (5).

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED BUTANE (6)

Temperature		kPa	Pressure		Entropy from 255.37°K J/(mol·°K)		Enthalpy above 255.37°K kJ/mol		Latent Heat of Vaporization kJ/mol	Specific Volume m^3/kg		Density kg/m^3	
°K	°F		bar	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
255.37	0	50.332	0.504	0.497	0.000	89.981	0.000	23.036	23.036	0.001 62	0.693	617.3	1.443
260.93	10	63.432	0.634	0.626	2.675	89.981	0.743	23.508	22.765	0.001 63	0.559	613.5	1.789
266.48	20	79.979	0.799	0.789	5.350	90.224	1.419	23.981	22.562	0.001 65	0.451	606.1	2.217
272.04	30	99.284	0.993	0.980	8.025	90.224	2.162	24.522	22.360	0.001 66	0.368	602.4	2.717
277.59	40	122.037	1.22	1.204	10.700	90.224	2.905	24.995	22.090	0.001 68	0.305	595.2	3.279
283.15	50	148.926	1.49	1.470	13.619	90.710	3.648	25.467	21.819	0.001 70	0.254	588.2	3.937
288.71	60	181.332	1.81	1.790	16.294	90.953	4.458	26.008	21.550	0.001 71	0.212	584.8	4.717
294.26	70	217.874	2.18	2.150	18.969	91.197	5.202	26.481	21.279	0.001 73	0.180	578.0	5.556
299.82	80	259.242	2.59	2.559	21.644	91.440	6.012	26.954	20.942	0.001 75	0.154	571.4	6.494
305.37	90	306.816	3.07	3.028	24.319	91.683	6.890	27.426	20.536	0.001 77	0.131	565.0	7.634
310.93	100	359.905	3.60	3.552	26.994	91.926	7.701	27.899	20.198	0.001 79	0.113	558.7	8.850
316.48	110	419.200	4.19	4.137	29.669	92.413	8.579	28.440	19.861	0.001 81	0.098 6	552.5	10.142
322.04	120	488.147	4.88	4.818	32.588	92.899	9.457	28.845	19.388	0.001 84	0.086 2	543.5	11.601
327.59	130	561.231	5.61	5.539	35.263	93.385	10.336	29.318	18.982	0.001 86	0.075 5	537.6	13.245
333.15	140	638.452	6.38	6.301	38.181	93.872	11.281	29.858	18.577	0.001 89	0.066 8	529.1	14.970

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED BUTANE (7)

H, ENTHALPY, kJ/mol; **S**, ENTROPY, J/(mol·°K); **V**, SPECIFIC VOLUME, m^3/kg

Pressure kPa	Pressure bar	atm		Temperature, °K 294.26	310.93	327.59	344.26	360.93	377.59
			H	22.559	24.114	25.721	27.382	29.092	30.855
101.325	1.013 25	1.000	S	82.587 6	87.718 9	92.753 0	97.689 8	102.553 6	107.344 4
			V	0.402 7	0.427 4	0.451 8	0.476 1	0.500 2	0.524 3
			H	22.476	24.046	25.662	27.331	29.048	30.818
137.897	1.38	1.361	S	79.742 3	84.922 2	90.004 9	94.966 0	99.829 8	104.620 7
			V	0.292 2	0.311 0	0.329 2	0.347 3	0.365 3	0.383 1
			H		23.749	25.415	27.117	28.865	30.664
275.789	2.76	2.722	S		78.599 3	83.827 9	88.886 2	93.847 3	98.735 5
			V		0.149 2	0.159 1	0.168 8	0.178 2	0.187 5
			H			25.130	26.882	28.667	30.495
413.684	4.14	4.083	S			79.839 5	85.043 8	90.126 5	95.087 6
			V			0.102 1	0.109 1	0.115 8	0.123 9
			H			24.808	26.629	28.452	30.314
551.579	5.52	5.444	S			76.775 3	82.101 2	87.305 5	92.388 2
			V			0.073 4	0.079 2	0.084 6	0.089 7
			H				26.360	28.224	30.114
689.473	6.90	6.805	S				79.620 7	84.970 9	90.175 2
			V				0.061 1	0.065 7	0.070 1
			H					27.924	29.842
861.842	8.62	8.506	S					82.441 7	87.816 2
			V					0.050 5	0.054 4
			H					27.610	29.550
1 034.210	10.34	10.207	S					80.374 6	85.724 8
			V					0.040 3	0.043 8
			H						29.240
1 206.578	12.07	11.908	S						83.779 2
			V						0.036 2
			H						28.911
1 378.947	13.79	13.609	S						81.955 3
			V						0.030 2
			H						28.563
1 551.315	15.51	15.310	S						80.398 9
			V						0.025 5

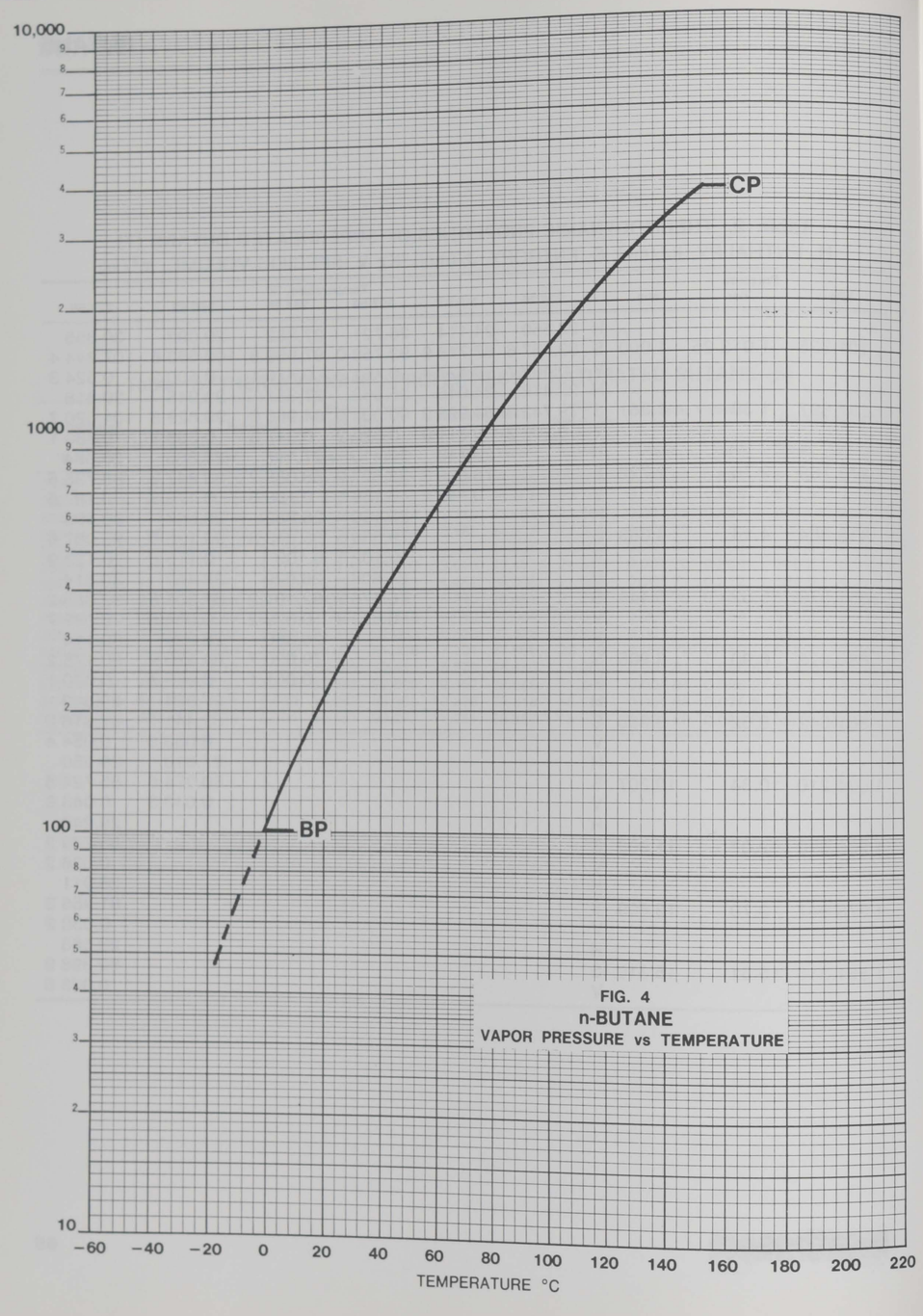


FIG. 4
n-BUTANE
VAPOR PRESSURE vs TEMPERATURE

1-BUTENE

(Synonym: alpha-Butylene)
(Formula: $CH_3CH_2CH{:}CH_2$ or C_4H_8)

PHYSICAL PROPERTIES (1)

Molar Mass	0.056 108 kg
Molecular Weight	0.056 108 kg
One Mole of C_4H_8	418.2 dm^3/kg; 6.7 ft^3/lb
Specific Volume @ 21.1 °C, 101.325 kPa	263.4 kPa; 2.63 bar; 38.2 psia; 2.6 atm
Vapor Pressure @ 21.1 °C	266.89 °K; −6.3 °C; 20.7 °F
Boiling Point @ 101.325 kPa	87.80 °K; −185.4 °C; −301.6 °F
Triple Point	2.365 5 kg/m^3
Absolute Density, Gas @ 101.325 kPa @ 25 °C	2.00
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	0.680 kg/l
Density, Liquid @ −40 °C	419.55 °K; 146.4 °C; 295.5 °F
Critical Temperature	4 023 kPa; 40.23 bar; 583.4 psia; 39.7 atm
Critical Pressure	4.295 dm^3/kg
Critical Volume	0.233 kg/dm^3
Critical Density	0.278
Critical Compressibility Factor	3 848.4 J/mol; 919.8 cal/mol
Latent Heat of Fusion @ −185.4 °C	1.6–9.3% (by volume)
Flammable Limits In Air	
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	87.329 kJ/(kmol·°K); 87.329 J/(mol·°K) 0.372 kcal/(kg·°C)
@ Constant Volume	79.113 kJ/(kmol·°K); 79.113 J/(mol·°K) 0.337 kcal/(kg·°C)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C Cp/Cv	1.104
Specific Heat, Liquid @ −20 °C	127.003 J/(mol·°K) 0.541 kcal/(kg·°C)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.007 63 mPa·s; 0.007 63 $mN·s/m^2$; 0.007 63 cP
Viscosity, Liquid @ −40 °C	0.272 mPa·s; 0.272 $mN·s/m^2$ 0.272 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.014 44 W/(m·°K); 34.5×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −40 °C	0.145 6 W/(m·°K); 348.0×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 0 °C	15.6 mN/m; 15.6 dyn/cm
Refractive Index, Liquid, n_D @ −25 °C	1.377 7
Heat of Combustion, Gas @ 25 °C and Constant Pressure	
Gross, to form H_2O (liq) + CO_2 (gas)	2 717.3 kJ/mol
Net, to form H_2O (gas) + CO_2 (gas)	2 541.2 kJ/mol
Heat of Combustion, Liquid @ 25 °C and Constant Pressure	
Gross, to form H_2O (liq) + CO_2 (gas)	2 696.9 kJ/mol
Net, to form H_2O (gas) + CO_2 (gas)	2 520.9 kJ/mol

Description

1-Butene is a colorless, flammable gas at room temperature and atmospheric pressure. It is very soluble in alcohol and ether, and insoluble in water. It is readily liquefied and is shipped as a liquefied petroleum gas in low pressure steel cylinders under its own vapor pressure of 162 kPa (23.5 psig) at 21.1 °C.

Specifications

Matheson supplies two grades of 1-butene, as follows:

1. Research Grade

This grade of 1-butene is of the highest purity available. Although there is no minimum purity specification, this grade has a typical purity of 99.9 mole %. Small amounts of isobu-

tylene and 1,3-butadiene are present as impurities. This grade is furnished with a statement of purity.

2. C. P. Grade

This grade has a minimum purity of 99.0 mole %.

Uses

1-Butene is a member of the alkene group of hydrocarbons. Alkenes serve as intermediates in the preparation of a variety of organic compounds. Sulfuric acid and sulfur dioxide react with alkenes to give alkyl hydrogen sulfates and alkyl sulfonates, respectively, many of which are useful as detergents. In the industrially important Oxo process, alkenes react catalytically with carbon monoxide and hydrogen to give aldehydes. Alkenes are polymerized by heating with catalysts to give high-octane gasolines, plastics, and synthetic rubber. Alkanes react with alkenes in the presence of catalysts to form motor fuels in a process known as alkylation.

Toxicity (2)

1-Butene is nontoxic; at higher concentrations it can act as an anesthetic. It possesses stronger anesthetic properties than ethylene or propylene. 1-Butene is about 4.5 times as toxic as ethylene.

Contact of the skin with liquid 1-butene may cause frostbite.

First Aid Treatment (2)

Inhalation

The conscious person who becomes aware of any symptoms such as rapid respiration, air hunger, diminished mental alertness, muscular incoordination, faulty judgment, emotional instability, rapid fatigue, nausea and vomiting should go promptly to an uncontaminated area and inhale fresh air or oxygen. However, in the event of massive exposure, the victim may become unconscious or symptoms of asphyxiation may persist. In that case, the person should be removed promptly to an uncontaminated atmosphere and given artificial respiration if necessary and then oxygen, after breathing has been restored. Treat symptomatically thereafter.

Skin Contact

If contact of the liquid form of 1-butene with the skin occurs, frostbite may develop. In case frostbite develops, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The hazards due to the handling of 1-butene stem mainly from its extreme flammability. Store and use 1-butene cylinders in well-ventilated areas away from heat and all ignition sources such as flames and sparks. Never use flames to detect flammable gas leaks, use soap water solution. Do not use 1-butene around sparking motors or other nonexplosion-proof equipment. Do not store reserve stocks of 1-butene cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all lines and equipment used with 1-butene.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

All fittings and joints should be painted with soap water solution to detect leaks, which will be indicated by bubble formation. Never use a flame to detect leaks.

Disposal of Leaking Cylinders

Leaking cylinders of 1-butene may be disposed of by the procedure described in Appendix II-A.

Materials of Construction

Since 1-butene is a noncorrosive gas, any common or commercially available metal may be used. However, piping systems or vessels to contain 1-butene should be designed to have a working pressure as specified by competent engineers using a safety factor conforming to the ASME code for pressure piping.

Cylinder and Valve Description

DOT approved cylinders containing 1-butene are usually of the low pressure type having a rated service pressure of 1 034 kPa (150 psig) or higher. Cylinders of 1-butene are equipped with valves having Compressed Gas Association (CGA) valve outlet No. 510 having a thread size of 0.885 inch diameter-14 threads per inch, left-hand internal threads accepting a bullet-shaped nipple. See Figure 1 for illustration of the valve outlet and mating connection. This valve outlet is standard for all liquefied petroleum gases. Valves used in this service by Matheson are of the diaphragm type and contain no packing. They are therefore leak-free and require no packing adjustments. Lecture bottles have a special $^{5}/_{16}$"-32 threads per inch female outlet and $^{9}/_{16}$"-18 threads per inch male dual valve outlet.

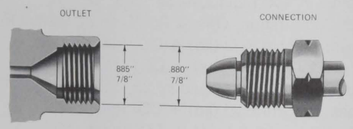


Fig. 1. CONNECTION 510 .885"-14 LH INT. accepting a Bullet Shaped Nipple.

Safety Devices

A number of different safety devices are permitted on cylinders containing 1-butene. A frangible disc is allowed in cylinders have a minimum required test pressure of 20 684 kPa (3 000 psig) or higher, and is required in only one end of the container. A 73.9 °C (165 °F) fusible metal may be used; however, when cylinders are over 30 inches long (exclusive of the neck) this device is required in both ends. A frangible disc backed up with 73.9 °C (165 °F) fusible metal is permitted in cylinders having a minimum required test pressure of 20 684 kPa (3 000 psig) or higher and when cylinders are over 30 inches long (exclusive of the neck) this device is required at both ends. The most commonly used safety device, which is employed by Matheson, is the spring-loaded safety relief valve. If cylinder pressure becomes dangerously high, usually due to overheating, the safety relief device will open (at approximately 2586 kPa (375 psig)) and release 1-butene gas until the pressure returns to a safe level.

Recommended Controls

Automatic Pressure Regulators

Satisfactory pressure regulation can be obtained with Matheson single stage regulator Model 1P-510. This regulator has a brass body, brass internal parts, fabric-reinforced neoprene rubber diaphragm, and a delivery pressure range of 28–240 kPa (4–35 psig).

Satisfactory pressure regulation can also be obtained with a low pressure regulator. For low pressure regulation Matheson supplies a Model 70 regulator. The regulator has an oversize pancake body of die cast aluminum, Buna N diaphragm, rubber seat and brass needle valve outlet, ¼" NPT male, and hose connection. The delivery pressure range of this regulator is 3.4–34.5 kPa (0.5–5 psig).

This regulator is designed primarily for liquefied petroleum gases where it is particularly suited for fuel gas burner operation, since its steady low pressure delivery permits a stable flame to be obtained. It is ideal for use with flame photometers.

Regulator Model 3321 is recommended for use with lecture bottles. It has a delivery pressure range of 28–410 kPa (4–60 psig).

Manual Controls

Matheson needle valve Model 50-510, a brass bar stock valve, is available for direct connection to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as ¼" compression fitting, ¼" NPT male or female pipe, or a serrated hose end. It should be used only where supervised flow is available and should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. A Model 31B manual needle valve is available for use with lecture bottles.

Flowmeters

Flowmeters of the rotameter type, such as Matheson 7600 or 7200 Series laboratory brass flowmeter units, are recommended where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

1-Butene is classified by the DOT as a flammable, compressed gas and is shipped with the required "Red Gas Label".

Chemical Preparation

1-Butene is produced by both thermal and catalytic cracking of petroleum and natural gas fractions, and by catalytic dehydrogenation of butane, followed by separation and purification processes. It has also been produced by polymerization of ethylene, but this method is not competitive with the first two methods.

Chemical Properties

1-Butene is a member of the alkene (olefin) series of hydrocarbons. The alkenes being unsaturated will undergo a wide variety of addition reactions. Some of the general reactions of alkenes are as follows:

(a) The alkenes combine with hydrogen halides forming alkyl halides, the descending order of reactivity being HI, HBr, HCl. Normal addition follows Markownikoff's rule, the halogen atom becoming attached to the carbon carrying the fewest hydrogen atoms. Peroxides reverse the direction of addition of hydrogen bromide to alkenes, but not of hydrogen chloride and hydrogen iodide which add in the normal way, whether a peroxide is present or absent. Reaction of higher alkenes, (e.g., 1-butene) with hydrogen chloride is slow and requires catalysis.

(b) The alkenes combine with halogens; the order of decreasing addition rate being chlorine, bromine, iodine. At higher temperatures, substitution on the carbon adjacent to the doubly bonded carbon atoms can occur.

(c) The alkenes are hydrogenated to the corresponding alkanes in the presence of suitable catalysts (platinum, palladium, Raney nickel).

(d) The alkenes combine with concentrated sulfuric acid forming alkyl hydrogen sulfates which, on hydrolysis, yield alcohols. The method is a convenient one for the hydration of double bonds.

(e) With positive halogen compounds, like N-bromosuccinimide, the alkenes are halogenated at the alpha carbon—allylic halogenation.

(f) With hypochlorous acid, the alkenes give chlorohydrins.

(g) In the presence of aluminum chloride, the alkenes combine with acyl halides giving halogeno ketones.

(h) The alkenes combine with carbon monoxide and hydrogen in the presence of cobalt under high pressure to form aldehydes.

(i) The alkenes are readily oxidized by a variety of oxidizing agents, such as potassium permanganate, hydrogen peroxide, perbenzoic acid, and others.

(j) The alkenes can be polymerized to polyalkenes under suitable conditions, the polymerization being catalyzed by aluminum chloride or boron trifluoride.

(k) At elevated temperatures and pressures, and in the presence of sulfuric acid or other catalysts, alkanes may add to alkenes.

(l) The alkenes may be isomerized by heating alone or in the presence of catalysts.

Thermodynamic and Detailed Physical Data

Molecular Structure

The formation of the double bond in 1-butene occurs by trigonal hybridization. As a result strong σ-bonds are formed between the two ethylenic carbon atoms and between the same two carbon atoms and the three attached hydrogen atoms and the ethyl group. There remains an unchanged 2p orbital of each ethylenic carbon atom and these two 2p orbitals interact to form a π-bond between the two ethylenic carbon atoms. Thus the double bond between carbon atoms consists of an σ-bond and a π-bond. The two bonds are of unequal strength, the σ-bond being stronger than the π-bond. There is no free rotation about the double bond as there is about a single σ-bond. The presence of the ethyl group in this ethylenic system would tend toward a partial displacement of the shared electrons to the methylene group.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous 1-butene.

Vapor Pressure (3)

The vapor pressure of liquid 1-butene between −67 and 40 °C is represented by the following Antoine vapor pressure equation:

$$\log_{10} p = A - \frac{B}{t + c}$$

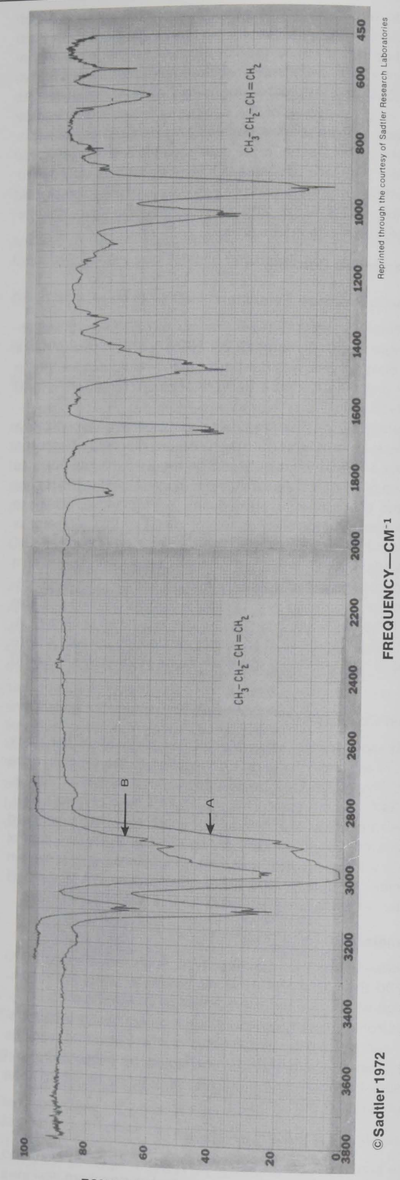
in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.842 90, 926.1, and 240.0, respectively.

Some vapor pressure values calculated by the above equation are shown below.

Temperature, °C	Vapor Pressure kPa	mbar	mmHg
−60	6.65	66.5	49.9
−40	21.74	217.4	163.1
−20	57.32	573.2	429.9
0	128.04	1 280.4	960.4
20	254.6	2 546	1 910
40	457.4	4 574	3 431

Vapor pressure values which have been reported between 30 and 125 °C are shown below.

Temperature, °C	Vapor Pressure kPa	bar	atm
30	345.5	3.46	3.410
50	596.7	5.97	5.889



Reprinted through the courtesy of Sadtler Research Laboratories
©Sadtler 1972

Fig. 2. Infrared spectrum of gaseous 1-butene; 10 cm path length cell, with KBr windows; curve A obtained at a cell pressure of 5.333 kPa (40 mmHg); curve B at 1.067 kPa (8 mmHg) (7).

Temperature, °C	Vapor Pressure kPa	bar	atm
75	1 075.6	10.76	10.61
100	1 790.9	17.91	17.675
125	2 815.2	28.15	27.784

For additional vapor pressure data, see Table 1 and Figure 3.

Latent heat of vaporization, ΔHv (4).

Temperature, °C	ΔHv, kJ/mol
−60	24.767
−40	23.898
−20	23.194
−6.26	21.917
0	21.668
25	20.377
40	19.367

Thermodynamic Data

Thermodynamic Properties of 1-Butene as Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	89.328 J/(mol·°K)
	21.350 cal/(mol·°C)
Entropy, S°	307.440 J/(mol·°K)
	73.480 cal/(mol·°C)
Free Energy Function, $(F_T^\circ - H_0^\circ)/T$	−248.195 J/(mol·°K)
	−59.320 cal/(mol·°C)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	17.673 kJ/mol
	4.224 kcal/mol
Enthalpy of Formation, ΔH_f°	−0.126 kJ/mol
	−0.03 kcal/mol
Free Energy of Formation ΔF_f°	71.505 kJ/mol
	17.09 kcal/mol

REFERENCES

[1] For extensive tabulations of thermodynamic and physical properties of 1-butene, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1974*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, pp. 11–16, *1977*, Matheson, Lyndhurst, New Jersey.

[3] F. D. Rossini, *et al.*, *Selected Values of Properties of Hydrocarbons and Related Compounds, 1953*, American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pennsylvania.

[4] R. W. Gallant, *Physical Properties of Hydrocarbons, 1968*, Volume 1, p. 17, Gulf Publishing Co., Houston, Texas.

[5] O. E. Kilpatrick and K. E. Pitzer, *J. Research Natl. Bur. Stand. 37*, 163–169 (1946).

[6] J. Weber, *A.I.Ch.E. Journal 1*, 210 (1955).

[7] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED 1-BUTENE(6)

Temperature		Pressure			Entropy J/(mol·°K)		Enthalpy kJ/mol		Latent Heat of Vaporization kJ/mol	Specific Volume m^3/kg		Density kg/m^3	
°K	°F	kPa	bar	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
273.15	32	128.518	1.285	1.268	0.000	79.301	0.000	21.663	21.663	0.001 62	0.299 0	617.28	3.344 5
277.59	40	151.064	1.511	1.491	1.596	79.066	0.443	21.950	21.507	0.001 63	0.261 6	613.50	3.822 6
283.15	50	183.400	1.834	1.810	3.920	78.995	1.096	21.354	21.258	0.001 65	0.220 0	606.06	4.545 5
288.71	60	220.63	2.21	2.18	6.291	78.995	1.774	22.745	20.971	0.001 67	0.180 4	598.80	5.543 2
294.26	70	263.38	2.63	2.60	8.803	78.995	2.504	23.149	20.645	0.001 68	0.150 5	595.24	6.644 5
299.82	80	311.64	3.12	3.08	11.527	78.995	3.313	23.541	20.228	0.001 70	0.140 5	588.24	7.117 4
305.37	90	366.11	3.66	3.61	14.015	79.136	4.069	23.958	19.889	0.001 73	0.110 0	578.03	9.090 9
310.93	100	430.92	4.31	4.25	16.480	79.277	4.826	24.349	19.523	0.001 75	0.094 9	571.43	10.537 4
316.48	110	497.11	4.97	4.91	18.921	79.371	5.595	24.728	19.133	0.001 78	0.083 0	561.80	12.048 2
322.04	120	575.71	5.76	5.68	21.292	79.535	6.351	25.106	18.755	0.001 81	0.072 4	552.49	13.812 2
327.59	130	663.96	6.64	6.55	23.640	79.700	7.095	25.458	18.363	0.001 84	0.063 1	543.48	15.847 9
333.15	140	759.80	7.60	7.50	25.987	80.005	7.890	25.888	17.998	0.001 87	0.054 6	534.76	18.315 0
338.71	150	865.29	8.65	8.54	28.335	80.287	8.686	26.280	17.594	0.001 90	0.047 9	526.32	20.876 8
344.16	160	981.81	9.82	9.69	30.683	80.568	9.482	26.658	17.176	0.001 93	0.042 2	518.13	23.696 7
349.82	170	1 112.12	11.12	10.98	33.077	80.991	10.303	27.062	16.759	0.001 96	0.037 1	510.20	26.954 2
355.37	180	1 254.84	12.55	12.38	35.472	81.296	11.151	27.440	16.289	0.002 00	0.032 7	500.00	30.581 0
360.93	190	1 411.35	14.11	13.93	37.913	81.601	12.025	27.792	15.767	0.002 04	0.028 9	490.20	34.602 1
366.48	200	1 576.14	15.76	15.56	40.401	81.977	12.925	28.158	15.233	0.002 08	0.025 5	480.77	39.215 7
372.04	210	1 755.40	17.55	17.32	42.984	82.305	13.877	28.510	14.633	0.002 12	0.022 7	471.70	44.052 9
377.59	220	1 949.83	19.50	19.24	45.637	82.634	14.881	28.849	13.968	0.002 17	0.020 2	460.83	49.505 0
383.15	230	2 160.81	21.61	21.33	48.336	82.845	15.911	29.136	13.225	0.002 23	0.017 9	448.43	55.865 9
388.71	240	2 388.34	23.88	23.57	51.036	82.986	16.955	29.371	12.416	0.002 29	0.015 7	436.68	63.694 3
394.26	250	2 637.24	26.37	26.03	53.830	83.033	18.050	29.566	11.516	0.002 37	0.013 7	421.94	72.992 7
399.82	260	2 904.75	29.05	28.67	56.694	82.587	19.185	29.540	10.355	0.002 47	0.011 8	404.86	84.745 8
405.37	270	3 186.75	31.87	31.45	60.379	82.235	20.672	29.527	8.855	0.002 61	0.010 1	383.14	99.009 9
410.93	280	3.481.84	34.82	34.36	64.511	81.014	22.615	29.397	6.782	0.002 80	0.008 4	357.14	119.047 6

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED 1-BUTENE (6)

H, ENTHALPY, kJ/mol; **S**, ENTROPY, J/(mol·°K); **V**, SPECIFIC VOLUME, m^3/kg

Pressure kPa	Pressure bar	Pressure atm		Temperature, °K 273.15	277.59	299.82	322.04	344.26	366.48	388.71	410.93	433.15	455.37
101.325	1.013	1.000	H	21.741	22.093	23.971	26.006	28.158	30.283	32.618	34.979	37.613	40.287
			S	81.437	82.775	89.278	95.710	102.048	108.293	114.467	120.524	126.533	132.473
			V	0.384 3	0.391 5	0.426 4	0.461 0	0.494 9	0.528 6	0.562 2	0.595 6	0.629 3	0.661 1
172.368	1.72	1.701	H			23.815	25.875	28.040	30.192	32.527	34.900	37.548	40.221
			S			85.029	91.414	97.729	103.950	110.124	116.157	122.167	128.106
			V			0.246 0	0.266 9	0.287 5	0.307 5	0.327 5	0.347 4	0.367 2	0.386 9
344.737	3.45	3.402	H				25.562	27.779	29.957	32.318	34.705	37.378	40.078
			S				84.982	91.414	97.729	103.950	110.077	116.134	122.097
			V				0.127 9	0.139 2	0.150 0	0.106 5	0.170 9	0.181 1	0.191 2
517.105	5.17	5.103	H				25.171	27.453	29.670	32.070	34.457	37.183	39.908
			S				80.850	87.447	93.879	100.170	106.133	112.472	118.481
			V				0.081 5	0.089 6	0.097 4	0.104 8	0.112 1	0.119 2	0.126 0
689.473	6.89	6.805	H					27.114	29.384	31.822	34.235	36.987	39.739
			S					84.324	90.897	97.306	103.363	109.748	115.805
			V					0.064 8	0.071 0	0.077 0	0.082 7	0.088 1	0.093 4
1 034.210	10.34	10.207	H						28.758	31.314	33.831	36.596	39.387
			S						86.179	92.869	99.278	105.687	111.861
			V						0.044 5	0.048 8	0.054 1	0.056 9	0.060 7
1 378.947	13.79	13.609	H						28.288	30.972	33.361	36.191	39.035
			S						82.869	89.278	95.921	102.541	108.856
			V						0.031 0	0.034 7	0.038 2	0.041 5	0.044 4
2 068.420	20.68	20.414	H							29.736	32.409	35.318	38.291
			S							84.301	90.804	97.611	104.255
			V							0.020 0	0.023 0	0.025 7	0.028 0
2 757.893	27.58	27.218	H								31.144	34.248	37.457
			S								86.249	93.222	100.429
			V								0.014 9	0.017 4	0.019 7
3 447.367	34.47	34.023	H								29.527	32.879	36.478
			S								81.484	89.184	96.387
			V								0.008 8	0.012 4	0.014 5
4 136.840	41.37	40.827	H									31.327	35.331
			S									84.770	93.245
			V									0.008 5	0.010 9
4 826.313	48.26	47.632	H									29.005	33.974
			S									78.291	89.465
			V									0.005 4	0.008 2
5 515.787	55.16	54.437	H										32.383
			S										85.404
			V										0.006 0

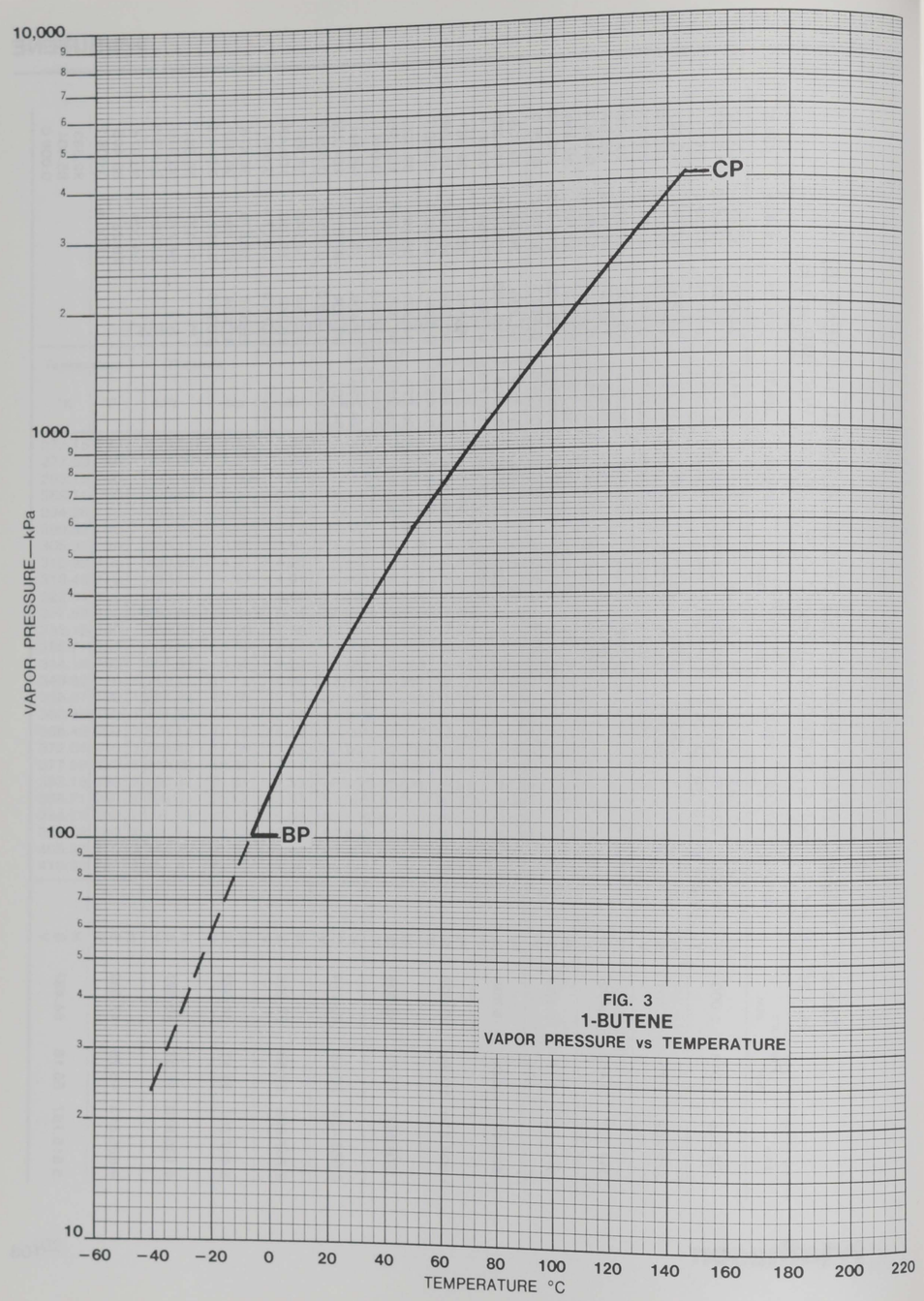


FIG. 3
1-BUTENE
VAPOR PRESSURE vs TEMPERATURE

CIS-2-BUTENE

(Formula: $CH_3CH{:}CHCH_3$ or C_4H_8)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.056 108 kg
One Mole of C_4H_8	0.056 108 kg
Specific Volume @ 21.1 °C @ 101.325 kPa	418.3 dm^3/kg; 6.7 ft^3/lb
Vapor Pressure @ 21.1 °C	191.0 kPa; 1.91 bar; 27.7 psia; 1.88 atm
Boiling Point @ 101.325 kPa	276.87 °K; 3.7 °C; 38.7 °F
Freezing Point	134.24 °K; −138.9 °C; −218.0 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	2.406 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	1.997
Density, Liquid @ Saturation Pressure @ 25 °C	0.615 4 kg/l
Critical Temperature	435.55 °K; 162.4 °C; 324.3 °F
Critical Pressure	4 205 kPa; 42.05 bar; 609.9 psia; 41.5 atm
Critical Volume	4.171 dm^3/kg
Critical Density	0.240 kg/dm^3
Critical Compressibility Factor	0.272
Latent Heat of Fusion @ −138.9 °C	130.271 kJ/kg; 31.136 kcal/kg
Flammability Limits In Air	1.6–9.7% (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	90.616 kJ/(kmol·°K); 90.616 J/(mol·°K); 0.386 kcal/(kg·°C)
@ Constant Volume	82.399 kJ/(kmol·°K); 82.399 J/(mol·°K); 0.351 kcal/(kg·°C)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C Cp/Cv	1.100
Molar Specific Heat, Liquid @ 0 °C	125.125 J/(mol·°K); 29.906 cal/(mol·°C)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.007 53 mPa·s; 0.007 53 $mN·s/m^2$; 0.007 53 cP
Viscosity, Liquid @ −20 °C	0.270 mPa·s; 0.270 $mN·s/m^2$; 0.270 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.032 0 W/(m·°K); 7.65 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −20 °C	0.031 1 W/(m·°K); 74.3 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −20 °C	18.8 mN·m; 18.8 dyn/cm
Refractive Index, Liquid, n_D @ −25 °C	1.384 2
Heat of Combustion, Gas @ 25 °C and Constant Pressure	
Gross, to form H_2O (liq) + CO_2 (gas)	2 706.2 kJ/mol; 646.8 kcal/mol
Net, to form H_2O (gas) + CO_2 (gas)	2 534.37 kJ/mol; 605.73 kcal/mol
Heat of Combustion, Liquid @ 25 °C and Constant Pressure	
Gross, to form H_2O (liq) + CO_2 (gas)	2 688.26 kJ/mol; 642.51 kcal/mol
Net, to form H_2O (gas) + CO_2 (gas)	2 510.20 kJ/mol; 600.43 kcal/mol

Description

cis-2-Butene is a colorless, flammable gas at room temperature and atmospheric pressure. It is readily liquefied and is shipped as a liquefied petroleum gas in low pressure cylinders under its own vapor pressure of 90 kPa (13 psig) at 21.1 °C.

Specification

Matheson has a Tech Grade of cis-2-butene, with a purity of 95.0% (min).

Uses

cis-2-Butene is a member of the alkene group of hydrocarbons. Alkenes serve as intermediates in the preparation of a variety of organic compounds. Sulfuric acid and sulfur dioxide react with alkenes to give alkyl hydrogen sulfates and alkyl sulfonates, respectively, many of which are useful as detergents. In the industrially important Oxo process, alkenes react catalytically with carbon monoxide and hydrogen to give aldehydes. Alkenes are polymerized by heating with catalysts to give high-octane gasolines, plastics, and synthetic rubber. Alkanes react with alkenes in the presence of catalysts to form motor fuels in a process known as alkylation.

Toxicity (2)

cis-2-Butene is nontoxic, and is classified as a simple asphyxiant. At higher concentrations it can act as an anesthetic; it possesses stronger anesthetic properties than ethylene or propylene. It is about 4.5 times as toxic as ethylene.

Contact of the skin with the liquid form of cis-2-butene may cause frostbite.

First Aid Treatment (2)

Inhalation

The conscious person who becomes aware of any symptoms such as rapid respiration, air hunger, diminished mental alertness, muscular incoordination, faulty judgement, emotional instability, rapid fatigue, nausea and vomiting should go promptly to an uncontaminated area and inhale fresh air or oxygen. However, in the event of massive exposure, the victim may become unconscious or symptoms of asphyxiation may persist. In that case, the person should be removed promptly to an uncontaminated atmosphere and given artificial respiration if necessary and then oxygen, after breathing has been restored. Treat symptomatically thereafter.

Skin Contact

If contact of the liquid form of cis-2-butene with the skin occurs, frostbite may develop. In case frostbite develops, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit next to his body. Then place the frostbitten part in warm water, about 42°C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The hazards due to the handling of cis-2-butene stem mainly from its extreme flammability. Store and use cis-2-butene cylinders in well-ventilated areas away from heat and all ignition sources such as flames and sparks. Never use flames to detect flammable gas leaks; use soap water solution. Do not use cis-2-butene around sparking motors or other non-explosion proof equipment. Do not store reserve stocks of cis-2-butene with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all lines and equipment used with cis-2-butene.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

All fittings and joints should be painted with soap water solution to detect leaks, which will be indicated by bubble formation. Never use a flame to detect leaks.

Disposal of Leaking Cylinders

Leaking cylinders should be disposed of by the procedure described in Appendix II-A.

Materials of Construction

Since cis-2-butene is a noncorrosive gas any common or commercially available metal may be used. However, piping systems or vessels to contain cis-2-butene should be designed to have a working pressure as specified by competent engineers using a safety factor conforming to the ASME code for pressure piping.

Cylinder and Valve Description

DOT approved cylinders containing cis-2-butene are usually of the low pressure type having a rated service pressure of 1 034 kPa (150 psig) or higher. Cylinders of cis-2-butene are equipped with valves having Compressed Gas Association (CGA) valve outlet No. 510 having a thread size of 0.885 inch diameter-14 threads per inch, left-hand internal threads accepting a bullet-shaped nipple. See Figure 1 for illustration of the valve outlet and mating connection. The valve outlet is standard for all liquefied petroleum gases. Valves used in this service by Matheson are of the diaphragm type and contain no packing. They are, therefore, relatively leak-free and require no packing adjustments. Lecture bottles have a special 5/16"-32 threads per inch male dual valve outlet.

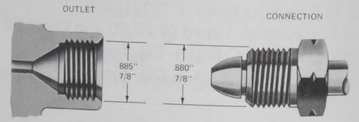


Fig. 1. CONNECTION 510 .885"-14 LH INT. accepting a Bullet Shaped Nipple

Safety Devices

A number of different safety devices are permitted on cylinders containing cis-2-butene. A frangible disc is allowed in cylinders having a minimum required test pressure of 20 684 kPa (3 000 psig) or higher, and is required in only one end of the container. A 73.9 °C (165 °F) fusible metal may be used; however, when cylinders are over 30 inches long, exclusive of the neck, this device is required in both ends. A frangible disc backed up with 73.9 °C (165 °F) fusible metal is permitted in cylinders having a minimum required test pressure of 20 684 kPa (3 000 psig) or higher and when cylinders are over 30 inches long (exclusive of the neck) this device is required at both ends. The most commonly used safety device, and the one employed by Matheson, is the spring-loaded safety relief valve. If cylinder pressure becomes dangerously high, usually due to overheating, the safety relief device will open (at approximately 2 586 kPa (375 psig)) and release cis-2-butene gas until the pressure again returns to a safe level.

Recommended Controls

Automatic Pressure Regulators

Satisfactory pressure regulation can be obtained with Matheson single stage regulator Model 1P-510, which has a delivery pressure range of 28–240 kPa (4–35 psig). Satisfactory pressure regulation can also be obtained with a low pressure regulator. Matheson supplies a Model 70 regulator constructed of a forged aluminum body, Buna N diaphragm, rubber seat and brass needle valve outlet, ¼" NPT male, and hose connection. The delivery pressure range of this regulator is 3.4–34.5 kPa (0.5–5.0 psig).

This regulator is designed primarily for liquefied petroleum gases where it is particularly suited for fuel gas burner operation, since its steady low pressure delivery permits a stable flame to be obtained.

Regulator Model 3321 is recommended for use with lecture bottles.

Manual Controls

Matheson needle valve Model 50-510 is a brass bar stock valve that is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets (¼ inch compression fitting or ¼ inch male or female NPT pipe) but is commonly supplied with a serrated hose end. It should be used only where manual flow control is needed and should not be used as a pressure control, since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. A Model 31B manual needle valve can be supplied for use with lecture bottles where accurate flow control is desired.

Flowmeters

Flowmeters of the rotameter type, such as Matheson 7600 or 7200 Series laboratory brass flowmeter units, are recommended where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes. Flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

cis-2-Butene is classified by the Department of Transportation as a flammable, compressed gas and is shipped with the required "Red Gas Label".

Commercial Preparations

cis-2-Butene is produced by both thermal and catalytic cracking of petroleum and natural gas fractions and by catalytic dehydrogenation of butane, followed by separation and purification processes. cis-2-Butene can also be obtained by heating 1-butene in a quartz tube at 550 °C (87% conversion) or in a limestone-filled porcelain tube at 420 °C (20% conversion).

Chemical Properties

cis-2-Butene is a member of the alkene or olefin series of hydrocarbons. The alkenes being unsaturated will undergo a wide variety of addition reactions. Some of the general reactions of alkenes are as follows:

(a) The alkenes combine with hydrogen halides forming alkyl halides, the descending order to reactivity being HI, HBr, HCl. Normal addition follows Markownikoff's rule, the halogen atom becoming attached to the carbon carrying the fewest hydrogen atoms. Peroxides reverse the direction of the addition of hydrogen bromide to alkenes.

(b) The alkenes combine with halogens; the order of decreasing addition rate being chlorine, bromine, iodine. At higher temperatures, substitution on the carbon adjacent to the doubly bonded carbon atoms can occur.

(c) The alkenes are hydrogenated to the corresponding alkanes in the presence of suitable catalysts (platinum, palladium, Raney nickel).

(d) The alkenes combine with concentrated sulfuric acid forming alkyl hydrogen sulfates which, on hydrolysis, yield alcohols. The method is a convenient one for the hydration of double bonds.

(e) With positive halogen compounds (like N-bromosuccinimide) the alkenes are halogenated at the alpha carbon—allylic halogenation.

(f) With hypochlorous acid, the alkenes give chlorohydrins.

(g) In the presence of aluminum chloride, the alkenes combine with acyl halides giving halogeno ketones.

(h) The alkenes combine with carbon monoxide and hydrogen in the presence of cobalt under high pressure to form aldehydes.

(i) The alkenes are readily oxidized by a variety of oxidizing

agents, such as potassium, permanganate, hydrogen peroxide, perbenzoic acid and others.

(j) The alkenes can be polymerized to higher alkenes under suitable conditions, the polymerization being catalyzed by aluminum chloride or boron trifluoride.

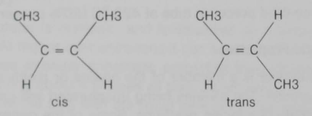
(k) At elevated temperatures and pressures, and in the presence of sulfuric acid or other catalysts, alkanes may add to alkenes.

(l) The alkenes may be isomerized by heating alone or in the presence of catalysts.

Thermodynamic and Detailed Physical Data

Molecular Structure

As described for 1-butene, the double bond in cis-2-butene occurs by trigonal hybridization. As before, the double bond consists of an σ-bond and a π-bond. In the case of cis-2-butene, however, the substituents on each of the ethylenic carbon atoms are different (in 1-butene one carbon atom has the same substituents: hydrogen). As a result, geometrical isomerism can occur with cis-2-butene but not with 1-butene. In the cis isomer of cis-2-butene both methyl groups are on the same side of the double bond, while in the trans form the methyl groups are on opposite sides of the double bond:



Both forms are quite stable since interconversion occurs only at relatively high temperatures or by irradiation with light of suitable wavelength.

Infrared Spectra

See Figure 2 for the infrared spectrum of gaseous cis-2-butene.

Vapor Pressure

The vapor pressure of cis-2-butene between −59 and 41 °C is represented by the following Antoine vapor pressure equation (3):

$$\log_{10} p = A - \frac{B}{t + c}$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.869 26, 960.1, and 237.0, respectively.

Some vapor pressure values calculated by this equation are shown below:

Temperature, °C	Vapor Pressure kPa	mbar	mmHg
−60	3.72	37.2	27.9
−40	13.20	132.0	99.0
−20	37.10	371.0	278.3
0	87.74	877.4	658.1
20	181.3	1 813	1 360
40	337.4	3 374	2 531

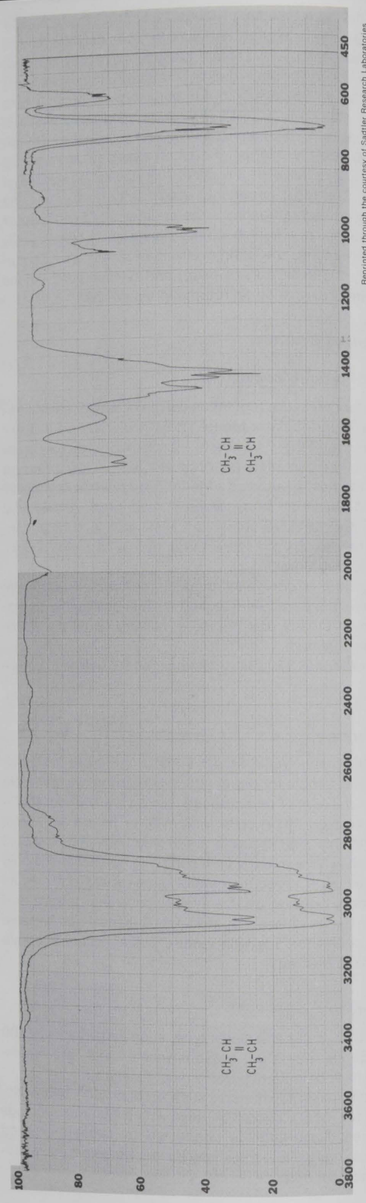


Fig. 2. Infrared spectrum of cis-2-butene; 10 cm path length cell, with kBr windows; curve A obtained at a cell pressure of 10.0 kPa (75 mmHg), curve B at 3.3 kPa (25 mmHg) (5).

See Figure 3 for the vapor pressure curve above 101.325 kPa.

The vapor pressure of cis-2-butene from 4.44 °C to its critical temperature (162.40 °C) is as follows (4):

Temperature, °C	Vapor Pressure kPa	bar	atm
4.44	104	1.04	1.03
10	129	1.29	1.27
20	180	1.80	1.78
40	335	3.35	3.31
60	578	5.78	5.70
80	924	9.24	9.12
100	1 400	14.0	13.79
120	2 020	20.2	19.92
162.40	4 200	42.0	41.50

See Figure 4 for the vapor pressure curve below 101.325 kPa. For comparison, the curve for trans-2-butene is included.

Latent Heat of Vaporization, ΔHv

Temperature, °C	ΔHv, kJ/kg
4.7	416.14
25	395.39

Thermodynamic Data

Thermodynamic properties of saturated cis-2-butene are listed in Table 1.

Thermodynamic Properties of cis-2-butene as Ideal Gas @ 25 °C

Heat Capacity, C_p°	78.910 J/(mol·°K)
Entropy, S°	300.830 J/(mol·°K)
Free Energy Function, $(F_T^\circ - H_0^\circ)/T$	−245.475 J/(mol·°K)
Enthalpy Difference $H_T^\circ - H_0^\circ$	16.657 kJ/mol
Enthalpy of Formation, ΔH_f°	6.99 kJ/mol
Free Energy of Formation, ΔF_f°	65.86 kJ/mol

REFERENCES

[1] For extensive tabulations of cis-trans-2-butene, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1974*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp 11–16, Matheson, Lyndhurst, New Jersey.

[3] F. D. Rossini, *et al.*, *Selected Values of Properties of Hydrocarbons and Related Compounds, 1953*, American Petroleum Institute Research Project 44, Carneigie Press, Pittsburgh, Pennsylvania.

[4] K. H. Hachmuth, *A.I.Ch. E. Trans. 42*, 974–982 (1946).

[5] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[6] R. B. Scott, W. J. Ferguson, and F. G. Brickwedde, *J. Research Natl. Bur. Stand. 33*, 1–20 (1944).

Table 1. THERMODYNAMIC PROPERTIES OF THE SATURATED LIQUID AND VAPOR (6)

Temperature, °K	Pressure			Entropy J/(mol•°K)		Enthalpy Difference H_T-H_0° kJ/mol		Latent Heat of Vaporization kJ/mol	Specific Volume dm^3/kg Vapor	Density kg/m^3 Vapor
	kPa	bar	atm	Liquid	Vapor	Liquid	Vapor			
245	24.945	0.249	0.246	196.326	298.386	25.426	50.431	25.005		
250	31.957	0.320	0.315	198.672	297.707	26.007	50.766	24.759	1 156.4	0.865
255	40.477	0.405	0.399	200.978	297.090	26.591	51.100	24.509	938.7	1.065
260	50.716	0.507	0.501	203.262	296.546	27.180	51.433	24.253	765.6	1.306
265	63.715	0.637	0.629	205.518	296.058	27.773	51.765	23.992	615.5	1.625
270	77.327	0.773	0.763	207.746	295.620	28.371	52.096	23.725	509.8	1.962
275	94.272	0.943	0.930	209.957	295.244	28.973	52.428	23.455	421.7	2.371
280	113.951	1.14	1.125	212.140	294.913	29.582	52.759	23.177	351.0	2.849
285	136.722	1.37	1.349	214.312	294.643	30.196	53.090	22.894	302.7	3.304
290	162.853	1.63	1.607	216.455	294.408	30.816	53.423	22.607	254.5	3.929
295	192.718	1.93	1.902	218.588	294.228	31.441	53.755	22.314		
298.15	213.609	2.14	2.108	219.929	294.133	31.841	53.967	22.126		
300	226.648	2.27	2.237	220.709	294.094	32.074	54.089	22.015		

Matheson

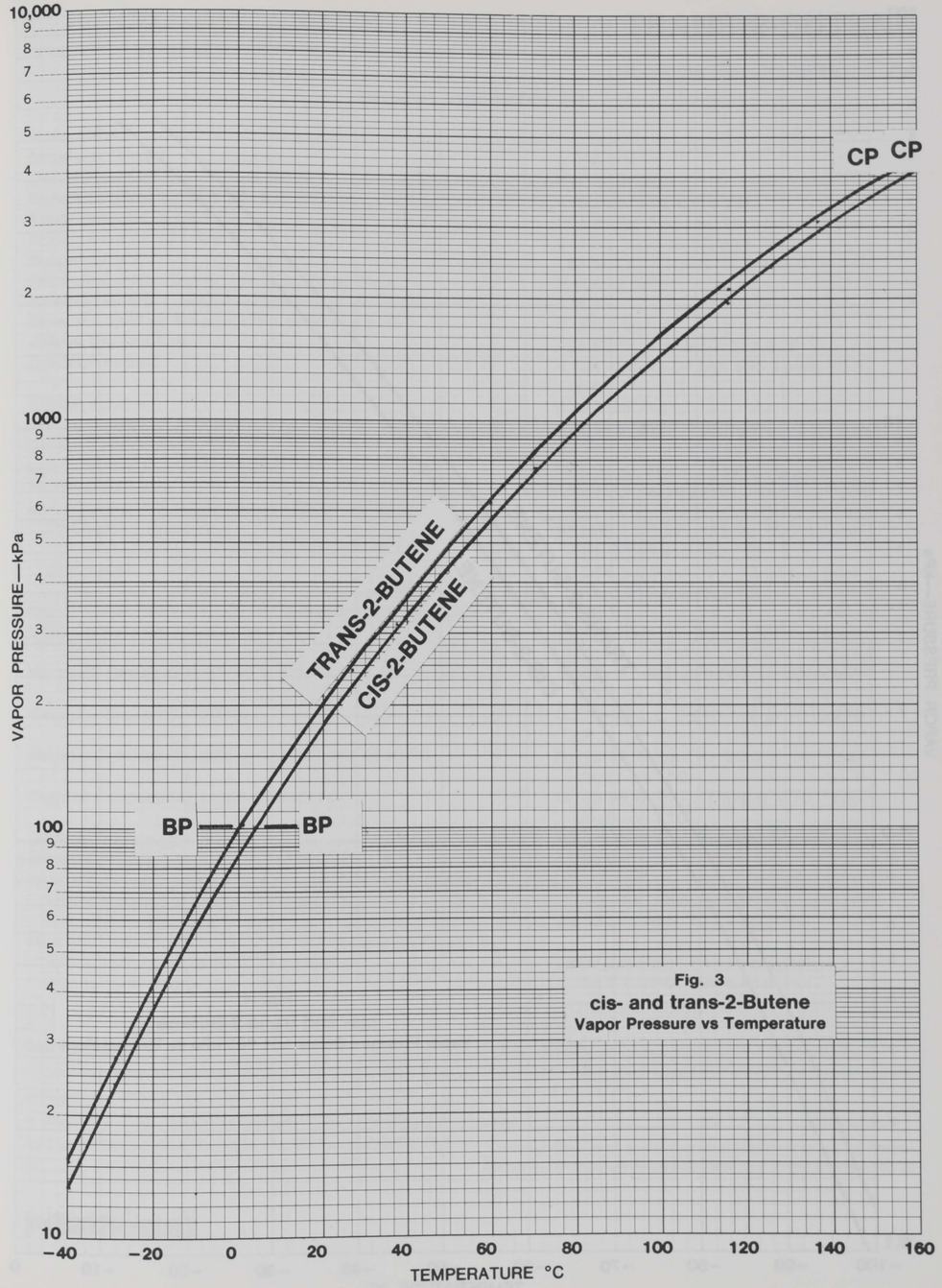


Fig. 3
cis- and trans-2-Butene
Vapor Pressure vs Temperature

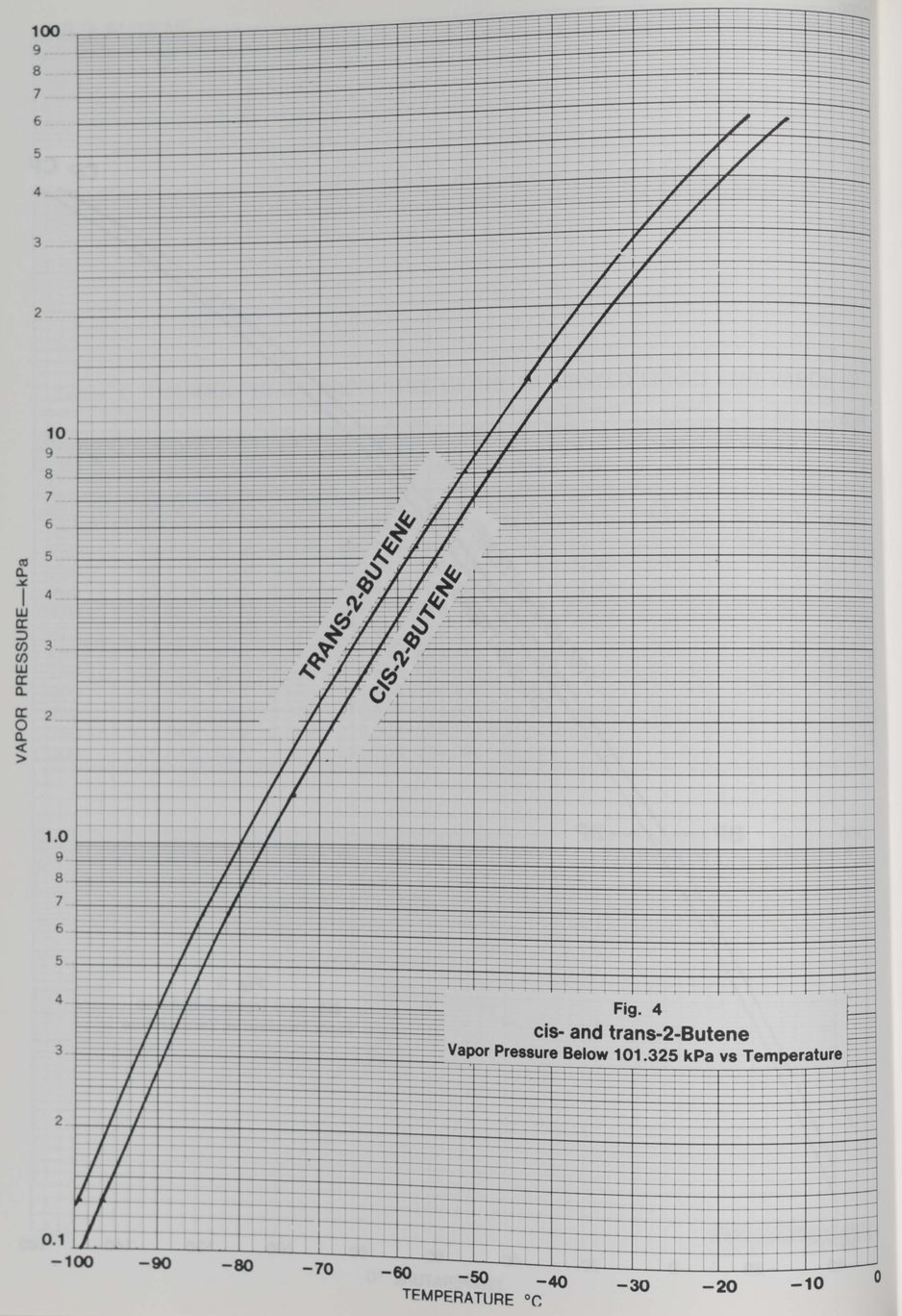


Fig. 4
cis- and trans-2-Butene
Vapor Pressure Below 101.325 kPa vs Temperature

TRANS-2-BUTENE

(Formula: $CH_3CH{:}CHCH_3$ or C_4H_8)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.056 108 kg
One Mole of C_4H_8	0.056 108 kg
Specific Volume @ 21.1 °C, 101.325 kPa	418.3 dm^3/kg; 6.7 ft^3/lb
Vapor Pressure @ 21.1 °C	204.8 kPa; 2.05 bar; 29.7 psia; 2.0 atm
Boiling Point @ 101.325 kPa	274.03 °K; 0.88 °C; 33.6 °F
Freezing Point	167.60 °K; −105.6 °C; −158.0 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	2.406 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	1.997
Density, Liquid @ Saturation Pressure @ 25 °C	0.598 4 kg/l
Critical Temperature	428.61 °K; 155.5 °C; 311.8 °F
Critical Pressure	4 104 kPa; 41.04 bar; 595.2 psia; 40.5 atm
Critical Volume	4.242 dm^3/kg
Critical Density	0.236 kg/dm^3
Critical Compressibility Factor	0.274
Latent Heat of Fusion @ −105.6 °C	97.567 kJ/mol; 23.319 kcal/mol
Flammability Limits In Air	1.6–9.7% (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	81.695 kJ/(kmol·°K); 81.695 J/(mol·°K); 0.348 kcal/(kg·°C)
@ Constant Volume	73.244 kJ/(kmol·°K); 73.244 J/(mol·°K); 0.312 kcal/(kg·°C)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C Cp/Cv	1.115
Molar Specific Heat, Liquid @ 0 °C	120.449 J/(mol·°K); 28.788 cal/(mol·°C)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.007 54 mPa·s; 0.007 54 $mN{\cdot}s/m^2$; 0.007 54 cP
Viscosity, Liquid @ −20 °C	0.270 mPa·s; 0.270 $mN{\cdot}s/m^2$; 0.270 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.013 39 W/(m·°K): 32.0×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −20 °C	0.135 98 W/(m·°K); 325.0×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −20 °C	20.2 mN/m; 20.2 dyn/cm
Refractive Index, Liquid, n_D @ −25 °C	1.393 2
Heat of Combustion, Gas @ 25 °C and Constant Pressure	
Gross, to form H_2O(liq) + CO_2(gas)	2 710.44 kJ/mol; 647.81 kcal/mol
Net, to form H_2O(gas) + CO_2(gas)	2 530.2 kJ/mol; 604.7 kcal/mol
Heat of Combustion, Liquid @ 25 °C and Constant Pressure	
Gross, to form H_2O(liq) + CO_2(gas)	2 684.7 kJ/mol; 641.7 kcal/mol
Net, to form H_2O(gas) + CO_2(gas)	2 508.6 kJ/mol; 599.6 kcal/mol

Description

trans-2-Butene is a colorless, flammable gas at room temperature and atmospheric pressure. It is readily liquefied and is shipped as a liquefied petroleum gas in low pressure cylinders under its own vapor pressure of 103 kPa (15 psig) at 21.1 °C.

Specifications

Matheson has a Tech Grade of trans-2-butene, with a minimum purity of 95.0%.

Uses

trans-2-Butene is a member of the alkene group of hydrocarbons. Alkenes serve as intermediates in the preparation of

a variety of organic compounds. Sulfuric acid and sulfur dioxide react with alkenes to give alkyl hydrogen sulfates and alkyl sulfonates, respectively, many of which are useful detergents. In the industrially important Oxo process, alkenes react catalytically with carbon monoxide and hydrogen to give aldehydes. Alkenes are polymerized by heating with catalysts to give high-octane gasolines, plastics and synthetic rubber. Alkanes react with alkenes in the presence of catalysts to form motor fuels in a process known as alkylation.

Toxicity (2)

trans-2-Butene is nontoxic and is classified as a simple asphyxiant. At higher concentrations they can at as an anesthetic; it possesses stronger anesthetic properties than ethylene or propylene. It is about 4.5 times as toxic as ethylene.

Contact of the skin with the liquid forms of trans-2-butenes may cause frostbite.

First Aid Treatment (2)

Inhalation

The conscious person who becomes aware of any symptoms such as rapid respiration, air hunger, diminished mental alertness, muscular incoordination, faulty judgment, emotional instability, rapid fatigue, nausea and vomiting should go promptly to an uncontaminated area and inhale fresh air or oxygen. However, in the event of massive exposure, the victim may become unconscious or symptoms of asphyxiation may persist. In that case, the person should be removed promptly to an uncontaminated atmosphere and given artificial respiration if necessary and then oxygen, after breathing has been restored. Treat symptomatically thereafter.

Skin Contact

If contact of the liquid form of trans-2-butene with the skin occurs, frostbite may develop. In case frostbite develops, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The hazards due to the handling of trans-2-butene stem mainly from its extreme flammability. Store and use trans-2-butene cylinders in well-ventilated areas away from heat and all ignition sources such as flames and sparks. Never use flames to detect flammable gas leaks; use soap water solution. Do not use trans-2-butene around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of trans-2-butene cylinders with cylinders containing oxygen, chlorine or other highly oxidizing or flammable materials. Ground all lines and equipment used with trans-2-butene.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

All fittings and joints should be painted with soap water solution to detect leaks, which will be indicated by bubble formation. Never use a flame to detect leaks.

Disposal of Leaking Cylinders

Leaking cylinders should be disposed of by the procedure described in Appendix II-A.

Materials of Construction

Since trans-2-butene is a noncorrosive gas, any common or commercially available metal may be used. However, piping systems or vessels to contain trans-2-butene should be designed to have a working pressure as specified by competent engineers using a safety factor conforming to the ASME code for pressure piping.

Cylinder and Valve Description

DOT approved cylinders containing trans-2-butene are usually of the low pressure type having a rated service pressure of 1 034 kPa (150 psig) or higher. Cylinders of trans-2-butene are equipped with valves having Compressed Gas Association (CGA) valve outlet No. 510 having a thread size of 0.885 inch diameter-14 threads per inch, left-hand internal threads accepting a bullet-shaped nipple. See Figure 1 for illustration of the valve outlet and mating connection. This valve outlet is standard for all liquefied petroleum gases. Valves used in this service by Matheson are of the diaphragm type and contain no packing. They are, therefore, relatively leak-free and require no packing adjustments. Lecture bottles have a special 5/16"-32 threads per inch, female outlet, and 9/16"-18 threads per inch male dual valve outlet.

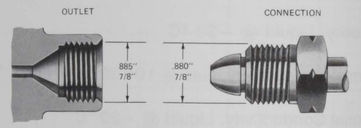


Fig. 1. CONNECTION 510 .885"-14 LH INT. accepting a Bullet Shaped Nipple

Safety Devices

A number of different safety devices are permitted on cylinders containing trans-2-butene. A frangible disc is allowed in cylinders having a minimum required test pressure of 20 684 kPa (3 000 psig) or higher, and is required in only one end of the container. A 73.9 °C (165 °F) fusible metal may be used; however, when cylinders are over 30 inches long (exclusive of the neck) this device is required in both ends. A frangible disc backed up with 73.9 °C (165 °F) fusible metal is permitted in cylinders having a minimum required test pressure of 20 684 kPa (3 000 psig) or higher and when cylinders are over 30 inches long (exclusive of the neck) this device is required at both ends. The most commonly used safety device, and the one employed by Matheson, is the spring-loaded safety relief valve. If cylinder pressure becomes dangerously high, usually due to overheating, the safety relief device will open (at approximately 2 586 kPa (375 psig)) and release trans-2-butene gas until the pressure again returns to a safe level.

Matheson

Recommended Controls

Automatic Pressure Regulators

Satisfactory pressure regulation can be obtained with Matheson single stage regulator Model 1P-510, which has a delivery pressure range of 28–240 kPa (4–35 psig). Satisfactory pressure regulation can also be obtained with a low pressure regulator. Matheson supplies a Model 70 regulator constructed of a forged aluminum body, Buna N diaphragm, rubber seat and brass needle valve outlet, ¼" NPT male, and hose connection. The delivery pressure range of this regulator is 3.4–34.5 kPa (0.5–5.0 psig).

This regulator is designed primarily for liquefied petroleum gases where it is particularly suited for fuel gas burner operation, since its steady low pressure delivery permits a stable flame to be obtained.

Regulator Model 3321 is recommended for use with lecture bottles.

Manual Valves

Matheson needle valve Model 50-510 is a brass bar stock valve that is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets (¼ inch compression fitting or ¼ inch male or female NPT pipe) but is commonly supplied with a serrated hose end. It should be used only where manual flow control is needed and should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. A Model 31B manual needle valve can be supplied for use with lecture bottles where accurate flow control is desired.

Flowmeters

Flowmeters of the rotameter type, such as Matheson 7600 or 7200 Series laboratory brass flowmeter units, are recommended where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes. Flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

trans-2-Butene is classified by the Department of Transportation as a flammable, compressed gas and is shipped with the required "Red Gas Label".

Commercial Preparation

trans-2-Butene is produced by both thermal and catalytic cracking of petroleum and natural gas fractions and by catalytic dehydrogenation of butane, followed by separation and purification processes. trans-2-Butene can also be obtained by heating 1-butene in a quartz tube at 550 °C (87% conversion) or in a limestone-filled porcelain tube at 420 °C (20% conversion).

Chemical Properties

trans-2-Butene is a member of the alkene or olefin series of hydrocarbons. The alkenes, being unsaturated, will undergo a wide variety of addition reactions. Some of the general reactions of alkenes are as follows:

(a) The alkenes combine with hydrogen halides forming alkyl halides, the descending order to reactivity being HI, HBr, HCl. Normal addition follows Markownikoff's rule, the halogen atom becoming attached to the carbon carrying the fewest hydrogen atoms. Peroxides reverse the direction of the addition of hydrogen bromide to alkenes.

(b) The alkenes combine with halogens; the order of decreasing addition rate being chlorine, bromine, iodine. At higher temperatures, substitution on the carbon adjacent to the doubly bonded carbon atoms can occur.

(c) The alkenes are hydrogenated to the corresponding alkanes in the presence of suitable catalysts (platinum, palladium, Raney nickel).

(d) The alkenes combine with concentrated sulfuric acid forming alkyl hydrogen sulfates which, on hydrolysis, yield alcohols. The method is a convenient one for the hydration of double bonds.

(e) With positive halogen compounds (like *N*-bromosuccinimide) the alkenes are halogenated at the alpha carbon (allylic halogenation).

(f) With hypochlorous acid, the alkenes give chlorohydrins.

(g) In the presence of aluminum chloride, the alkenes combine with acyl halides giving halogeno ketones.

(h) The alkenes combine with carbon monoxide and hydrogen in the presence of cobalt under high pressure to form aldehydes.

(i) The alkenes are readily oxidized by a variety of oxidizing agents, such as potassium permanganate, hydrogen peroxide, perbenzoic acid and others.

(j) The alkenes can be polymerized to higher alkenes under suitable conditions, the polymerization being catalyzed by aluminum chloride or boron trifluoride.

(k) At elevated temperatures and pressures, and in the presence of sulfuric acid or other catalysts, alkanes may add to alkenes.

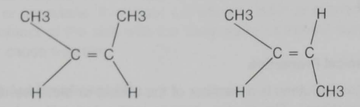
(l) The alkenes may be isomerized by heating alone or in the presence of catalysts.

Matheson

Thermodynamic and Detailed Physical Data

Molecular Structure

As described for 1-butene, the double bond in trans-2-butene occurs by trigonal hybridization. As before, the double bond consists of an σ-bond and a π-bond. In the case of trans-2-butene, however, the substituents on each of the ethylenic carbon atoms are different (in 1-butene one carbon atom has the same substituents: hydrogen). As a result, geometrical isomerism can occur with trans-2-butene but not with 1-butene. In the cis isomer of trans-2-butene both methyl groups are on the same side of the double bond, while in the trans form the methyl groups are on opposite sides of the double bond:



cis trans

Both forms are quite stable since interconversion occurs only at relatively high temperatures or by irradiation with light of suitable wavelength.

Infrared Spectra

See Figure 2 for infrared spectra of gaseous trans-2-butene.

Vapor Pressure

The vapor pressure of trans-2-butene between −62 °C and 49 °C is represented by the following Antoine vapor pressure equation:

$$\log_{10}P = A - \frac{B}{t + c}$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.869 52, 960.8, and 240.0, respectively.

See Figure 3 for the vapor pressure curve above 101.325 kPa.

The vapor pressure of trans-2-butene above 101.325 kPa is shown below:

Temperature, °C	Vapor Pressure kPa	bar	atm
0.88	101.325	1.013 25	1.00
10	142	1.42	1.40
20	200	2.00	1.97
40	366	3.66	3.61
60	627	6.27	6.19
80	1 000	10.00	9.87
100	1 531	15.31	15.11
154.85	4 154	41.54	41.00

See Figure 4 for the vapor pressure of trans-2-butene below 101.325 kPa. For comparison, the vapor pressure curve of cis-2-butene is included.

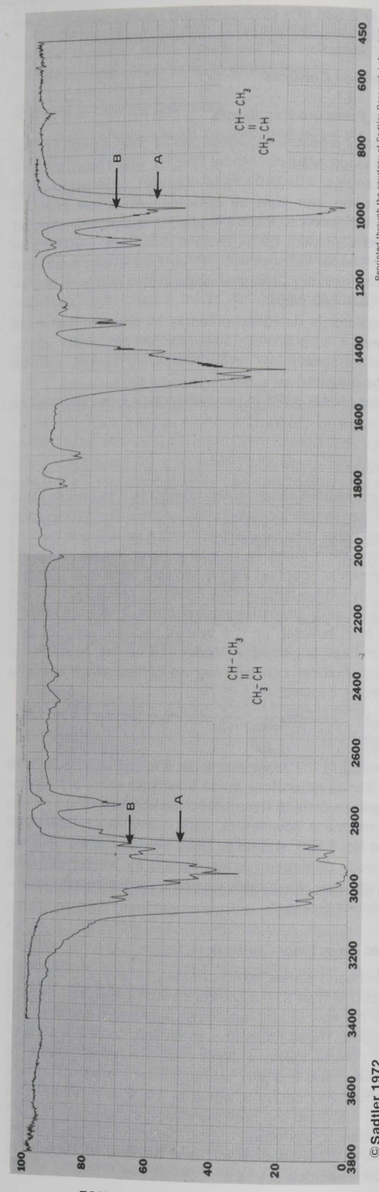


Fig. 2. Infrared spectrum of trans-2-butene; 10 cm path length cell, with KBr windows; curve A obtained at a cell pressure of 10.0 kPa (75 [mmHg]), curve B at 3.33 kPa (25 [mmHg]) (5).

Matheson

Latent Heat of Vaporization, ΔHv (4)

Temperature, °C	ΔHv, kJ/kg
−40	451.45
−20	432.63
0.88	405.60
20	392.46
25	384.09
40	369.03
60	342.67
80	309.20

Thermodynamic Properties of trans-2-butene as Ideal Gas @ 25 °C

Heat Capacity, C_p°	87.822 J/(mol·°K)
Entropy, S°	296.478 J/(mol·°K)
Free Energy Function, $(F_T^\circ - H_0^\circ)/T$	−237.651 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	17.531 kJ/mol
Enthalpy of Formation, ΔH_f°	−11.17 kJ/mol
Free Energy of Formation, ΔF_f°	62.97 kJ/mol

REFERENCES

[1] For extensive tabulations of cis-2-butene, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1974*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, 1977, pp. 11–16, Matheson, Lyndhurst, New Jersey.

[3] K. H. Hachmuth, *A.I.Ch.E. Trans 42*, 974–982 (1946).

[4] R. W. Gallant, *Physical Properties of Hydrocarbons, 1968*, Volume 1, p. 14, Gulf Publishing Co., Houston, Texas.

[5] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Matheson

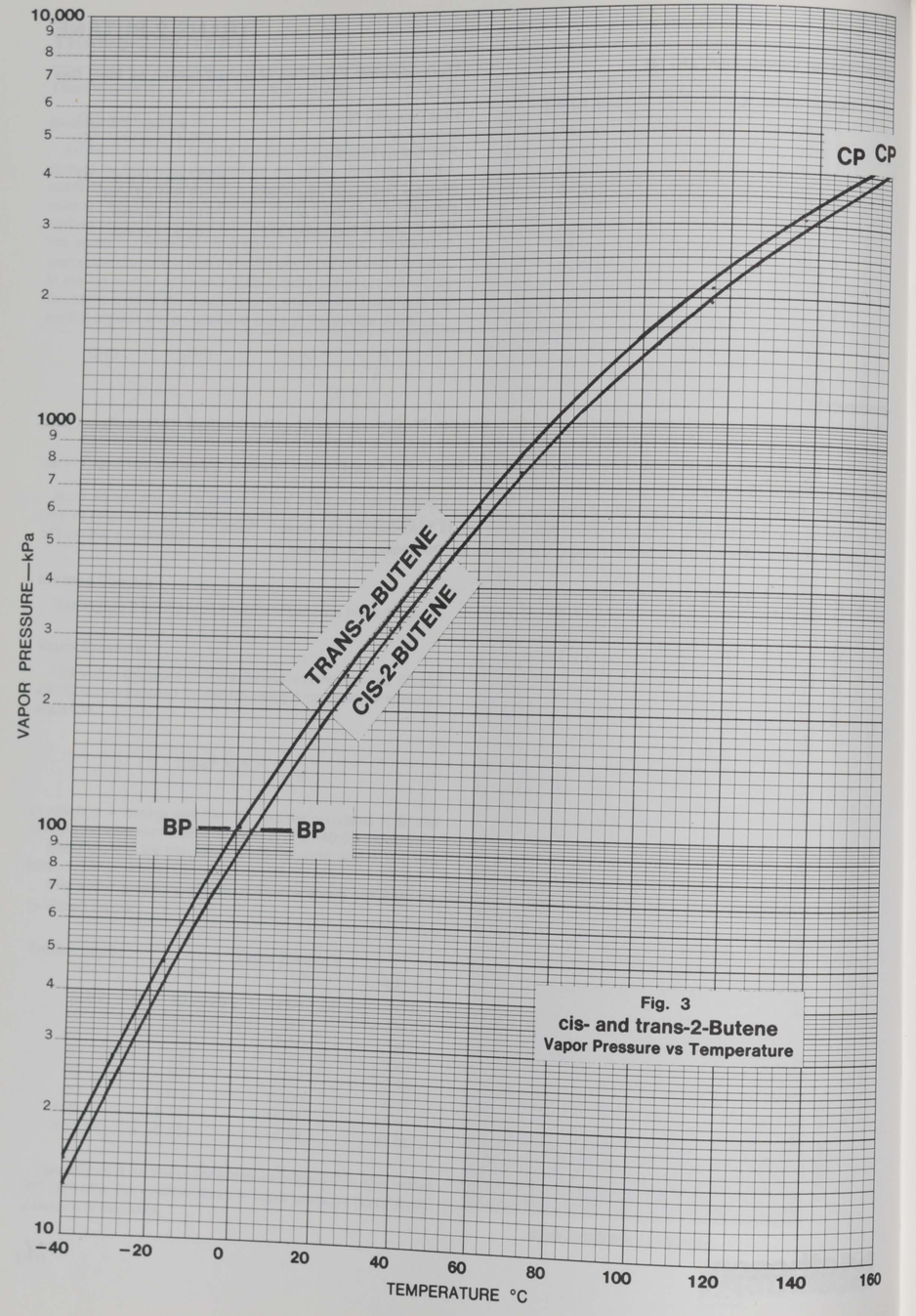


Fig. 3
cis- and trans-2-Butene
Vapor Pressure vs Temperature

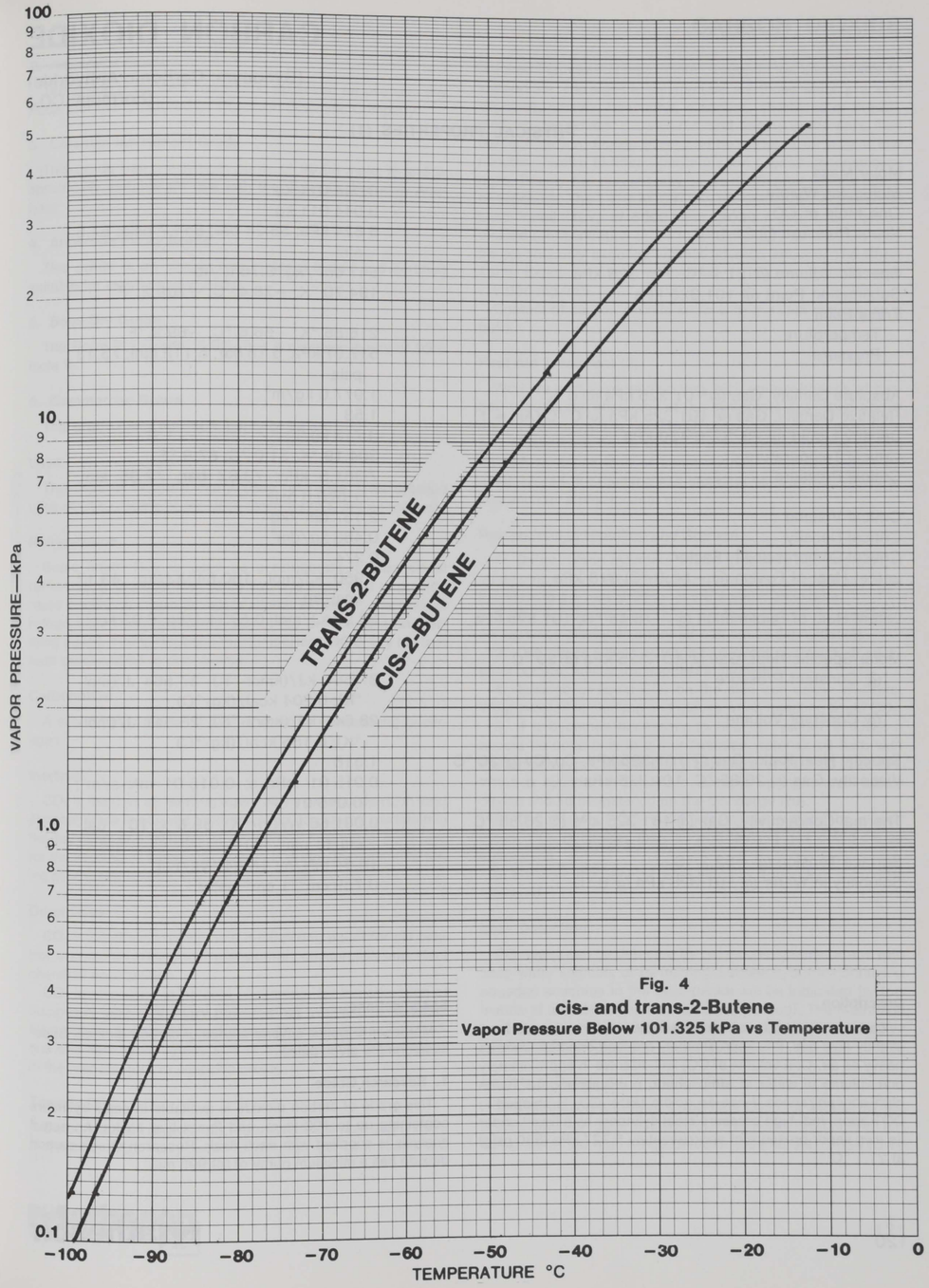


Fig. 4
cis- and trans-2-Butene
Vapor Pressure Below 101.325 kPa vs Temperature

CARBON DIOXIDE

(Synonym: Carbonic Anhydride)
(Formula: CO_2)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.044 011 kg
One Mole of CO_2	0.044 011 kg
Vapor Pressure @ 21.1 °C	5 824 kPa; 58.24 bar; 844.7 psia; 57.5 atm
Specific Volume @ 21.1 °C, 101.325 kPa	547 dm^3/kg; 8.76 ft^3/lb
Sublimation Point @ 101.325 kPa	194.70 °K; −78.4 °C; −109.2 °F
Triple Point	
Temperature	216.55 °K; −56.6 °C; −69.9 °F
Pressure	517.97 kPa; 5.18 bar; 5.112 atm; 75.13 psia
Absolute Density, Gas @ 101.325 kPa @ 0 °C	1.977 0 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 0 °C (Air = 1)	1.53
Density Liquid @ 25 °C, 6 430 kPa	0.713 kg/l
Critical Temperature	304.19 °K; 31.0 °C; 87.9 °F
Critical Pressure	7 381.5 kPa; 73.82 bar; 72.85 atm; 1 070.6 psia
Critical Volume	2.137 dm^3/kg
Critical Density	0.468 kg/dm^3
Critical Compressibility Factor	0.274
Latent Heat of Fusion @ −56.6 °C; 518 kPa	7.950 kJ/mol; 180.64 kJ/kg; 43.17 kcal/kg
Latent Heat of Sublimation @ −78.45 °C, 101.325 kPa	25.23 kJ/mol; 0.573 kJ/kg; 6.03 kcal/mol
Molar Specific Heat, Gas @ 101.325 kPa @ 20 °C	
@ Constant Pressure	37.564 kJ/(kmol·°K); 37.564 J/(mol·°K); 0.204 kcal/(kg·°C)
@ Constant Volume	28.541 kJ/(kmol·°K); 28.541 J/(mol·°K); 0.155 kcal/(kg·°C)
Specific Heat Ratio, Gas @ 101.325 kPa, Cp/Cv @ 20 °C	1.316
Viscosity, Gas @ 26.85 °C, 101.325 kPa	0.015 01 mPa·s; 0.015 01 $mN·s/m^2$; 0.015 01 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 26.85 °C	0.001 66 W/(m·°K); 39.6 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −52.2 °C	16.54 mN/m; 16.54 dyn/cm
Solubility In Water @ 101.325 kPa @ 0 °C	0.759 cm^3/1 cm^3 water

Description

Carbon dioxide is a nonflammable, colorless, odorless, slightly acid gas. It is approximately one and one-half times as heavy as air. One volume of CO_2 will dissolve in approximately one volume of water at atmospheric pressure and 15 °C. In high concentrations it has an acidic taste. CO_2 is shipped in DOT approved, high pressure steel cylinders as a liquid under its own vapor pressure of approximately 5 727 kPa (830 psig) at 21.1 °C.

Specifications

Matheson supplies several grades of carbon dioxide. Specifications are given below.

1. Research Grade

This grade of carbon dioxide is available in small cylinders containing up to 100 liters, and Pyrex liter flasks. An actual analysis is supplied with each flask. Research Grade carbon dioxide has a minimum purity of 99.995 min.

Matheson

2. Aquarator Grade

This grade is purified, tested and approved for use with the Aquarator manufactured by Precision Scientific Company.

3. Coleman Instrument Grade

This grade has a minimum purity of 99.99 mole % and is specifically suitable for use with the Coleman Nitrogen Analyzer.

4. Anaerobe Purity Grade

This grade is an oxygen-free material tested and certified suitable for use by anaerobists.

5. Bone Dry Grade

The Bone Dry Grade of CO_2 has a minimum purity of 99.8 mole %.

6. Commercial Grade

This grade has a minimum purity of 99.5%.

Uses

The uses of CO_2 are many. (See reference 1 for detailed uses of CO_2). Some of the uses listed for CO_2 are as follows:

Refrigeration

Some liquid CO_2 is used as a refrigerant in mechanical refrigerating systems and some liquid is expanded to provide rapid cooling for special applications. However, the bulk of refrigeration uses employing CO_2 utilize Dry Ice as a refrigerating agent. The largest and most important use of Dry Ice is in food preservation in distribution.

Carbonation

A substantial volume of CO_2 is used for carbonating beverages.

Inerting

CO_2 is used as an inerting agent in fire extinguishers, in inert atmospheres, in canned food products, to prevent oxidation in the handling and transfer of dangerous flammable materials, for the inerting of flammable materials during their manufacturing processes and for shielded arc welding.

Other Uses

CO_2 is used extensively as a neutralizing agent for pH control, in cement curing and in many other commercially important chemical applications.

CO_2 is also used in aerosol packaging, for the operation of equipment where ordinary power is not available or suitable, for pressure spraying in packaging, for the transfer of hazardous and flammable liquids and as a diluent with nitrous oxide in the manufacture of whipped cream.

Toxicity (2)

Carbon dioxide is generally regarded as a simple asphyxiant. Symptoms result only when such high concentrations are reached that there is insufficient oxygen in the atmosphere to support life. The signs and symptoms are those which precede asphyxia, namely, headache, dizziness, shortness of breath, muscular weakness, drowsiness, and ringing in the ears. Ten percent carbon dioxide in air can be endured for only a few minutes. Twelve to fifteen percent soon causes unconsciousness. Twenty-five percent may cause death after several hours of exposure. The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 5000 ppm (9000 mg/m^3) for carbon dioxide (concentration in air to which nearly all workers may be continuously exposed without adverse affects). The Short Term Exposure Limit established (STEL) is 15,000 ppm (18,000 mg/m^3).

Contact of carbon dioxide snow with the skin may cause a burn.

First Aid Treatment (2)

Workers who have inhaled very high concentrations of carbon dioxide and show any of the symptoms described above should be removed at once to an uncontaminated atmosphere and inhale fresh air or oxygen. If the exposure was severe enough to cause loss of consciousness, oxygen should be administered. If breathing has stopped, start artificial respiration and call a physician at once.

Precautions in Handling and Storage

1. Do not place cylinders where they may become part of an electric circuit. When electric arc welding, precautions must be taken to prevent striking an arc against a cylinder.
2. Do not discharge CO_2 in confined or poorly ventilated areas, since displacement of air can cause asphyxiation.
3. Use check valves or traps to prevent suckback. If suckback occurs, advise the supplier immediately.
4. Spillage of liquid CO_2 on the skin can cause frostbite. Wear protective clothing and gloves when handling liquid CO_2.
5. If it becomes necessary to heat a cylinder of CO_2, it should be done only in a thermostated water or oil bath with the temperature controlled to a maximum of 51.7 °C (125 °F). When a cylinder is heated a suitable spring-loaded safety device should be installed on the discharge line.
6. Do not store CO_2 cylinders in sub-surface or closed areas. CO_2 is heavier than air and leaking gas could cause suffocation.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

CO_2 leaks can be detected by painting suspected areas with soap water solution, or by holding a squeeze bottle containing aqueous ammonia in the area (leaks will be indicated by formation of a white ammonium carbonate cloud). The Matheson Leak Detectors Model 8016 and 8017 provide a more sensitive method of leak detection.

Analytical Detection

The Matheson-Kitagawa Toxic Gas Detector Model 8014K is available for determination of CO_2 concentrations in air. Using either the high range detector tube Model 126Sa (0.1–

Matheson

2.6%) or the low range detector tube Model 126Sb (100–7000 ppm), concentrations of carbon dioxide in the atmosphere produce a length of the stain in the detector tube which is read directly off the detector tube.

There are numerous volumetric, titrimetric, and gas chromatographic procedures available for determination of CO_2.

Disposal of Leaking Cylinders

If it becomes necessary to dispose of a leaking cylinder of carbon dioxide, the procedure described in Appendix II-C should be followed.

Materials of Construction

Dry CO_2 is a relatively inert gas and any common or commercially available metal may be used. However, piping systems or vessels to contain CO_2 should be designed to have a working pressure as specified by competent engineers using a safety factor conforming to the ASME code for pressure piping. When carbon dioxide is to be handled in aqueous systems it will form the weak acid, carbonic acid. Consequently materials resistant to this acid will have to be chosen.

Cylinder and Valve Description

CO_2 is shipped in DOT approved cylinders of the high pressure type having a minimum rated service of 12 410 kPa (1 800 psig). Cylinders of CO_2 are equipped with valves having a Compressed Gas Association (CGA) valve outlet connection No. 320 with an outlet thread size designated as 0.825 inch-14 threads per inch right-hand external with a flat face seating against a washer. See Figure 1 for an illustration of this valve outlet and its mating connection. Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet and 9/16 inch-18 threads per inch male dual valve outlet.

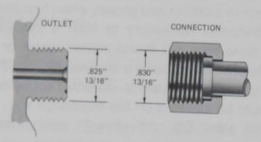


Fig. 1. CONNECTION 320 .825"-14 RH EXT. used with Flat Seat and Washer

Safety Devices

The only type of safety device permitted in CO_2 cylinders, for industrial purposes, is the frangible disc type. The frangible disc is contained in a special fitting and is an integral part of the cylinder valve. The frangible disc will burst at a pressure not exceeding the minimum required hydrostatic test pressure of the cylinder which is substantially below the bursting pressure of the cylinder. Bursting of the frangible disc results in the discharge of the entire cylinder contents.

Cylinder Contents

The Matheson Cylinder Scale Model 8510 is recommended for determining cylinder contents by weight.

Recommended Controls

Automatic Pressure Regulators

1. Single Stage Regulators

The single stage regulator will reduce cylinder pressure in one step to delivery pressure in a particular range depending upon the design of the regulator and its spring load. A single stage regulator will show a slight variation in delivery pressure as cylinder pressure falls. Since carbon dioxide is a liquefied gas at room temperature, the cylinder pressure will remain constant as long as any liquid remains in the cylinder. Therefore, a single stage regulator will give a steady delivery pressure, and tank pressure will not fall until approximately 80% of the cylinder content has been discharged. Above the critical temperature of 31.0 °C, carbon dioxide will convert completely to a gas and the discharge of gas will show a steady drop in pressure. The following single stage regulators are available from Matheson and are recommended for use with carbon dioxide:

Model No.	Delivery Pressure		
	kPa	bar (g)	psig
1L-320	28–550	0.28–5.5	4–80
1H-320	69–1 240	0.69–12.4	10–180
2-320	340–4 480	3.4–44.8	50–650
3320 (for lecture bottles)	28–410	0.28–4.1	4–60

These regulators are for use with the Coleman Instrument Grade, Bone Dry Grade, and Commercial Grade of carbon dioxide.

The following single stage regulators are recommended for use with the Research Purity Grade, Aquarator Grade and Anaerobe Purity Grade of carbon dioxide:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
19-320	28–340	0.28–3.4	4–50
3500-320	28–520	0.28–5.2	4–75

2. Two Stage Regulators

This type of regulator performs the same function as a single stage regulator. However, greater accuracy in the control of delivery pressure is maintained and the delivery pressure does not vary as cylinder pressure falls. The following two stage regulators are available from Matheson for use with carbon dioxide with Coleman Instrument Grade, Bone Dry Grade and Commercial Grade:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
8L-320	14–104	0.14–1.04	2–15
8-320	28–340	0.28–3.4	4–50
8H-320	69–690	0.69–6.9	10–100
9-320	138–1720	1.38–17.2	20–250

The following two stage regulators are recommended for use with the other grades of carbon dioxide:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
3800-320	28–620	0.28–6.2	4–90
3104-320	28–690	0.28–6.9	4–100

3. Low Pressure Regulator

Accurate low pressure regulation of carbon dioxide can be obtained by using a Matheson Model 70 regulator in series with a Model 1L-320 regulator. The Model 70 regulator has an oversize pancake body of die cast aluminum with a Buna N diaphragm. When the two regulators are used in series, they are connected together with a heavy duty hose and the proper fitting which are available. The delivery pressure range of this regulator is 3.4–34.5 kPa (0.5–5.0 psig).

Manual Controls

Manual needle valves for direct connection to the cylinder valve outlet are available. Those types of controls are mainly used for intermittent flows or where it is desired to control the flow of gas directly from the cylinder, but these types of controls require close supervision. They should not be used as pressure controls because dangerous pressures can develop if a line or system becomes plugged. Manual needle valves Model 50-320 or Model 52-320 with gauge to indicate tank pressure are recommended for use with carbon dioxide. These valves can be equipped with a serrated hose end, 1/4" compression fitting, or 1/4" NPT male or female outlets. The Model 31B or Model 30AR needle valve is recommended for use with lecture bottles. These needle valves are for use with the Coleman Instrument, Bone Dry, and Commercial Grades of carbon dioxide.

Manual control of the other grades of carbon dioxide can be obtained with needle valve Model 4351-320.

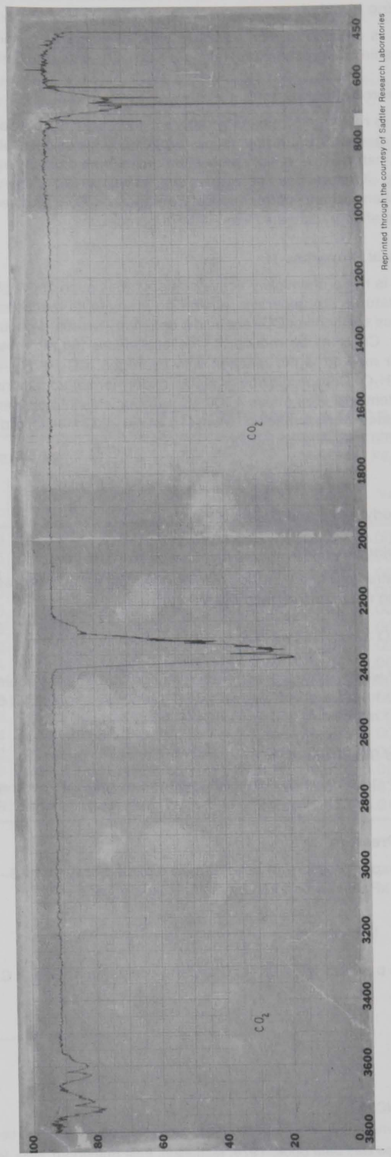
Flowmeters

In all cases where accurate flows of definite values must be known or reproduced it is recommended that Matheson Series 7600 or 7200 laboratory brass or stainless steel flowmeter units be used.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes and flow rates may be recorded from instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.



Reprinted through the courtesy of Sadtler Research Laboratories

©Sadtler 1972

Fig. 2. Infrared spectrum of gaseous carbon dioxide; 10 cm. path length, with KBr windows; cell pressure: 2.666 4 kPa (20 mmHg) (3).

Shipping Regulations

CO_2 is shipped in high pressure steel cylinders as a non-flammable compressed gas, taking a DOT "Green Label".

Commercial Preparations

CO_2 is recovered from many different sources. It is obtained as off-gases from fermentation processes, limestone kiln gases, natural CO_2 wells, combustion gases from coke ovens, burning of natural gas and various oils, as well as gas streams from chemical and petrochemical operations. CO_2 is purified and liquefied by at least seven different processes.

Chemical Properties

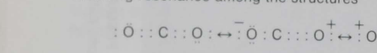
CO_2 is not a chemically active compound as such and high temperatures are generally required to promote its reactions. Aqueous solutions of CO_2 are acidic and many reactions occur readily. CO_2 may be reduced by several means but the most popular method is the reaction with hydrogen: $CO_2 + H_2 \rightarrow CO + H_2O$. Carbon dioxide is stable under normal conditions but at temperatures above 1700 °C it dissociates into oxygen and carbon monoxide to an extent (15.8% at 2227 °C) according to the following equation:

$$2CO_2 \rightarrow 2CO + O_2$$

Thermodynamic and Detailed Physical Data

Molecular Structure

The structure of the carbon dioxide molecule is described as involving resonance among the structures



each of which makes about equal contribution. The molecule belongs to point group $D_{\infty h}$ with C—O bond distance of 1.16×10^{-10} m (1.16 Å) and an O—C—O bond angle of 180°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous carbon dioxide.

Vapor Pressure

The vapor pressure of solid carbon dioxide between 1.33–199.98 kPa is represented by the following equation (3):

$$\log_{10} p = A - \frac{B}{t + C} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C and the constants A, B, and C have the values of 9.810 66, 1 347.786 and 273.0, respectively.

Some vapor pressure values calculated by this equation are shown below.

Temperature, °C	Vapor Pressure kPa	mbar	mmHg = tor
−120.03	1.333	13.3	10
−111.27	4.000	40.0	30
−102.56	10.67	106.7	80
−93.53	26.66	266.6	200
−83.48	66.66	666.6	500
−78.51	101.325	1 013.25	760
−76.43	119.99	1 199.9	900
−69.86	199.98	1 999.8	1 500

For additional vapor pressure values of the saturated solid, see Table 1.

For the vapor pressure of the saturated liquid, see Table 2.

For vapor pressure curve, see Figure 3.

Latent Heat of Vaporization, ΔHv(4)

Temperature, °C	ΔHv, kJ/kg
−56.57	0.369
25.00	0.121

For additional ΔHv values, see Table 2.

Thermodynamic Data

For thermodynamic properties of the saturated solid and vapor, see Table 1; for those of the saturated liquid and vapor, see Table 2; for those of the superheated vapor, see Table 3; for density, see Table 4; for compressibility factors, see Table 5.

Thermodynamic Properties of Carbon Dioxide as Ideal Gas @ 25 °C

Heat Capacity, C_p°	37.129 J/(mol·°K)
	0.844 kJ/(kg·°K)
Entropy, S°	213.685 J/(mol·°K)
	4.855 kJ/(kg·°K)
Free Energy Function, $(F^\circ_{298} - H^\circ_{298})/T$	−213.685 J/(mol·°K)
	−4.855 kJ/(kg·°K)
Enthalpy, H°	9.364 kJ/mol
	0.213 kJ/kg
Enthalpy of Formation, ΔH_f°	−393.522 kJ/mol
	−8.941 kJ/kg
Free Energy of Formation, ΔF_f°	−394.405 kJ/mol
	−8.962 kJ/kg

REFERENCES

[1] For extensive tabulations of thermodynamic and physical properties of carbon dioxide, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, 1974, Matheson, East Rutherford, New Jersey.

[2] W. Braker and A. L. Mossman, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, 1977, pp. 138–140, Matheson, Lyndhurst, New Jersey.

[3] *The Sadtler Standard Spectra*, 1972, Sadtler Research Laboratories, Inc. Philadelphia, Pennsylvania.

[4] B. J. Zwolinski, *et al*; *Selected Values of Properties of Chemical Compounds*, 1968, Volume 1, Texas A & M University, College Station, Texas.

[5] D. M. Newitt, *et al.*, in *Thermodynamic Functions of Gases*, F. Din, editor, 1962, Volume 1, p. 123, Butterwork Inc., Washington, D. C.

[6] See reference 5, pp. 128–134.

[7] J. Hilsenrath, *et al.*, *Tables of Thermal Properties of Gases*, 1955, pp. 155–160, Natl. Bur. Stand. Circ. 564, U. S. Government Printing Office, Washington, D. C.

[8] Ibid., pp. 149–154.

Table 1. THERMODYNAMIC PROPERTIES OF THE SATURATED SOLID AND VAPOR (5)

Temperature °K	Temperature °F	Pressure kPa	Pressure atm	Entropy kJ/(kg·°K) Solid	Entropy kJ/(kg·°K) Vapor	Enthalpy kJ/kg Solid	Enthalpy kJ/kg Vapor	Latent Heat of Sublimation kJ/kg	Specific Volume dm^3/kg Solid	Specific Volume dm^3/kg Vapor	Density kg/dm^3 Solid	Density kg/dm^3 Vapor
143.15	−202.00	0.308 03	0.003	041.216	5.411	92.479	693.121	600.642	0.615	87 815	1.626	0.000 011
148.15	−193.00	0.650 51	0.006	421.253	5.290	97.805	695.967	598.162	0.617	42 987	1.621	0.000 023
153.15	−184.00	1.308 11	0.012	911.289	5.176	103.211	698.644	595.433	0.619	22 099	1.616	0.000 045
158.15	−175.00	2.510 83	0.024	781.324	5.074	108.709	701.824	593.115	0.621	11 882	1.610	0.000 084
163.15	−166.00	4.617 38	0.045	571.359	4.978	114.290	704.753	590.463	0.623	6 650.8	1.605	0.000 150
168.15	−157.00	8.172 88	0.080	661.393	4.889	119.972	707.765	587.793	0.625	3 872.3	1.600	0.000 258
173.15	−148.00	13.972 7	0.137	9 1.427	4.805	125.758	710.778	585.020	0.627	2 326.7	1.595	0.000 430
178.15	−139.00	23.142 6	0.228	4 1.461	4.727	131.654	713.665	582.011	0.629	1 440.0	1.590	0.000 694
183.15	−130.00	37.267 3	0.367	8 1.494	4.655	137.654	716.636	578.982	0.632	917.25	1.582	0.001 090
188.15	−121.00	58.474 7	0.577	1 1.527	4.587	143.779	719.439	575.660	0.635	597.77	1.575	0.001 673
193.15	−112.00	89.622 0	0.884	5 1.560	4.520	150.038	721.907	571.869	0.639	397.67	1.565	0.002 515
198.15	−103.00	134.560	1.328	1.592	4.458	156.444	724.501	568.057	0.643	269.68	1.555	0.003 708
203.15	−94.00	198.090	1.955	1.624	4.399	162.992	726.593	563.601	0.647	185.68	1.546	0.005 386
208.15	−85.00	287.054	2.833	1.656	4.340	169.686	728.183	558.497	0.652	129.52	1.534	0.007 721
213.15	−76.00	409.758	4.044	1.689	4.279	176.548	728.602	552.054	0.657	91.228	1.522	0.010 962
216.55*	−69.88	517.973	5.112	1.720	4.247	181.318	728.476	547.158	0.661	72.220	1.513	0.013 847

* Triple point.

Table 2. THERMODYNAMIC PROPERTIES OF THE SATURATED LIQUID AND VAPOR (5)

Temperature °K	Temperature °F	Pressure kPa	Pressure atm	Entropy kJ/(kg·°K) Liquid	Entropy kJ/(kg·°K) Vapor	Enthalpy kJ/kg Liquid	Enthalpy kJ/kg Vapor	Latent Heat of Vaporization kJ/kg	Specific Volume dm^3/kg Liquid	Specific Volume dm^3/kg Vapor	Density kg/dm^3 Liquid	Density kg/dm^3 Vapor
216.55*	−69.88	519	5.112	2.639 3	4.246 8	380.242	728.476	348.234	0.849 0	72.220	1.177 9	0.013 85
218.15	−67.00	555	5.478	2.648 1	4.231 7	383.087	728.560	345.473	0.853 2	67.620	1.172 1	0.014 79
223.15	−58.00	684	6.747	2.689 1	4.200 3	392.250	729.522	337.272	0.866 9	55.407	1.153 5	0.018 05
228.15	−49.00	833	8.224	2.729 6	4.172 3	401.580	730.777	329.197	0.881 4	45.809	1.134 6	0.021 83
233.15	−40.00	1 006	9.928	2.770 2	4.146 3	411.036	731.949	320.913	0.896 9	38.164	1.115 0	0.026 20
238.15	−31.00	1 204	11.880	2.810 0	4.120 8	420.701	732.995	312.294	0.913 3	32.008	1.094 9	0.031 24
243.15	−22.00	1 429	14.103	2.849 3	4.097 0	430.492	733.915	303.423	0.930 9	27.001	1.074 2	0.037 04
248.15	−13.00	1 684	16.618	2.889 1	4.073 5	440.492	734.459	293.967	0.950 0	22.885	1.052 6	0.043 70
253.15	−4.00	1 971	19.449	2.928 8	4.050 1	450.700	734.501	283.801	0.971 0	19.466	1.029 9	0.051 37
258.15	5.00	2 292	22.617	2.968 5	4.025 8	461.160	734.041	272.881	0.993 9	16.609	1.006 1	0.060 21
263.15	14.00	2 649	26.147	3.008 3	4.001 1	471.872	733.120	261.248	1.018 3	14.194	0.982 0	0.070 45
268.15	23.00	3 046	30.065	3.048 5	3.974 8	483.001	731.321	248.320	1.045 5	12.141	0.956 5	0.082 37
273.15	32.00	3 485	34.397	3.089 9	3.947 6	494.632	728.895	234.263	1.075 9	10.383	0.929 5	0.096 31
278.15	41.00	3 969	39.172	3.132 6	3.912 0	506.933	723.706	216.773	1.113 0	8.718 4	0.898 5	0.114 70
283.15	50.00	4 501	44.425	3.176 9	3.876 1	520.029	718.016	197.987	1.158 4	7.374 6	0.863 3	0.135 60
288.15	59.00	5 086	50.192	3.224 6	3.840 5	534.255	711.782	177.527	1.213 0	6.222 8	0.824 4	0.160 70
293.15	68.00	5 727	56.525	3.276 1	3.797 8	550.070	703.038	152.968	1.290 3	5.157 3	0.775 0	0.193 90
298.15	77.00	6 433	63.487	3.343 0	3.753 0	570.321	691.364	121.043	1.402 5	4.132 2	0.713 0	0.242 00
303.15	86.00	7 211	71.166	3.451 4	3.655 6	602.119	663.959	61.840	1.686 1	2.910 4	0.593 1	0.343 60
304.19**	87.87	7 382	72.85	3.549 3	3.549 3	633.876	633.876	0.000	2.137 2	2.137 2	0.467 9	0.467 90

* Triple point; ** Critical point

Table 3. THERMODYNAMIC PROPERTIES OF SUPERHEATED CARBON DIOXIDE (6)

H, ENTHALPY, kJ/kg; **S**, ENTROPY, kJ/(kg·°K); **V**, SPECIFIC VOLUME, dm^3/kg

kPa	atm		Temperature, °K 193.15	213.15	233.15	253.15	273.15	293.15	313.15	333.15	353.15	373.15	393.15	413.15	423.15
5.066	0.5	H	723.665	739.104	754.919	770.986	787.345	804.081	821.152	838.641	856.423	874.582	893.075	911.777	921.233
		S	4.634 2	4.710 3	4.781 1	4.846 7	4.908 7	4.968 1	5.024 6	5.078 5	5.130 0	5.179 8	5.227 9	5.275 2	5.298 2
		V	710.94	788.73	864.30	939.82	1 015.08	1 090.21	1 165.22	1 240.13	1 314.98	1 389.77	1 464.55	1 539.22	1 576.70
101.325	1	H		737.597	753.789	770.149	786.718	803.579	820.733	838.206	856.172	874.414	892.907	911.610	921.108
		S		4.573 9	4.646 3	4.712 9	4.775 6	4.835 4	4.892 4	4.946 7	4.998 6	5.048 4	5.096 5	5.144 6	5.166 8
		V		390.59	429.45	467.83	505.81	543.65	581.36	618.98	656.54	694.05	731.54	769.03	787.76
303.98	3	H		731.698	749.354	766.802	784.082	801.529	819.144	836.967	855.00	873.410	892.071	910.982	920.480
		S		4.344 7	4.424 2	4.495 7	4.561 8	4.623 3	4.681 5	4.736 7	4.789 0	4.839 6	4.877 7	4.935 0	4.958 0
		V		125.54	139.65	153.09	166.24	179.23	192.10	204.88	217.58	230.23	242.86	255.49	261.80
506.63	5	H			744.794	763.287	781.362	799.353	817.386	835.545	853.829	872.448	891.276	910.271	919.852
		S			4.312 4	4.388 6	4.457 6	4.521 2	4.580 6	4.637 1	4.690 3	4.741 3	4.790 3	4.837 5	4.860 6
		V			81.63	90.14	98.31	106.34	114.25	122.05	129.78	137.47	145.13	152.79	156.61
1 013.25	10	H				754.208	774.375	793.788	812.909	831.905	850.858	869.937	889.142	908.472	918.221
		S				4.230 0	4.307 0	4.375 6	4.438 8	4.497 8	4.553 0	4.605 7	4.655 5	4.703 2	4.726 2
		V				42.77	47.29	51.63	55.82	59.90	63.93	67.90	71.84	75.76	77.72
2 026.5	20	H					758.476	781.446	803.202	824.039	844.415	864.582	884.539	904.539	914.581
		S					4.132 1	4.212 3	4.283 6	4.348 0	4.407 4	4.463 1	4.515 8	4.565 6	4.589 4
		V					21.58	24.14	26.54	28.79	30.96	33.09	35.18	37.24	38.27
4 053	40	H						751.990	780.902	806.131	829.813	852.448	874.247	895.460	905.836
		S						4.000 7	4.101 6	4.179 0	4.246 3	4.306 2	4.364 3	4.417 9	4.443 0
		V						10.07	11.72	13.16	14.47	15.69	16.86	17.99	18.55
6 080	60	H							754.292	785.546	813.035	838.474	862.364	885.125	896.129
		S							3.940 1	4.050 1	4.131 3	4.198 6	4.263 1	4.320 4	4.346 3
		V							6.538	7.855	8.918	9.868	10.76	11.60	12.00
8 106	80	H							711.657	758.852	792.868	822.282	849.017	873.954	885.795
		S							3.777 7	3.932 1	4.056 0	4.115 8	4.184 8	4.245 1	4.272 3
		V							3.440	5.106	6.112	6.948	7.697	8.391	8.722
10 133	100	H							622.161	721.656	768.726	804.248	834.666	862.113	875.084
		S							3.491 5	3.804 1	3.944 7	4.044 7	4.122 5	4.185 7	4.213 7
		V							1.555	3.383	4.418	5.216	5.884	6.481	6.763
20 265	200	H							582.455	637.265	686.343	730.485	771.781	811.194	830.398
		S							3.320 8	3.494 9	3.640 1	3.761 0	3.867 7	3.960 2	4.002 0
		V							1.190	1.381	1.660	2.041	2.454	2.837	3.011
30 398	300	H							573.836	619.148	659.859	698.519	736.677	775.044	794.374
		S							3.246 8	3.377 7	3.497 8	3.608 3	3.710 0	3.805 8	3.852 2
		V							1.092	1.199	1.335	1.500	1.690	1.900	2.009
40 530	400	H							570.739	612.203	649.440	685.214	720.987	757.388	776.006
		S							3.209 1	3.332 1	3.440 0	3.537 6	3.630 5	3.721 3	3.766 0
		V							1.043	1.121	1.210	1.312	1.430	1.564	1.638
50 663	500	H							570.405	609.567	645.005	678.812	712.661	747.346	765.212
		S							3.175 7	3.291 6	3.396 6	3.491 5	3.582 8	3.671 5	3.715 0
		V							1.005	1.067	1.137	1.215	1.301	1.395	1.445

Table 4. DENSITY OF GASEOUS CARBON DIOXIDE (7)

Temperature, °C	Unit: kg/m³ Pressure, kPa 10.1	101.3	405.3	709.3	1 013.2	4 053.0	7 092.8	10 132.5
−3	0.19879	2.00072	8.18023	14.6496	21.4465			
27	0.17886	1.79670	7.29829	12.9764	18.8448	93.947		
77	0.15328	1.53692	6.20343	10.9561	15.7982	70.134	139.276	235.500
127	0.13410	1.34317	5.40294	9.50838	13.6591	57.968	107.944	164.427
227	0.10727	1.07331	4.30314	7.54680	10.8043	44.140	78.779	114.541
327	0.08939	0.89414	3.57916	6.26788	8.96036	36.057	63.371	90.752
527	0.06704	0.67036	2.68042	4.68925	6.69630	26.672	46.426	65.903
727	0.05364	0.53622	2.14346	3.74859	5.35154	21.257	36.924	52.331
927	0.04469	0.44651	1.78602	3.12327	4.45833	17.698	30.730	43.549
1227	0.03576	0.35746	1.42878	2.49853	3.56671	14.159	24.596	34.872

Table 5. COMPRESSIBILITY FACTORS FOR CARBON DIOXIDE, Z = PV/RT (8)

Temperature, °C	Pressure, kPa 40.5	101.3	405.3	709.3	1 013.2	4 053	7 092.8	10 132.5
−23	0.99634	0.99085	0.9629	0.9337	0.9022			
27	0.99800	0.99501	0.9798	0.9644	0.9486	0.7611		
127	0.99927	0.99817	0.99267	0.98714	0.9185	0.9252	0.8697	0.8155
327	0.99990	0.99975	0.99903	0.99832	0.99763	0.9916	0.9874	0.9850
527	1.00004	1.00011	1.00046	1.00081	1.00118	1.0054	1.0108	1.0172
727	1.00008	1.0002	1.0008	1.0015	1.0022	1.0092	1.0167	1.0248
977	1.00010	1.0002	1.0010	1.0017	1.0025	1.0102	1.0181	1.0263
1227	1.00010	1.0002	1.0010	1.0018	1.0025	1.0100	1.0176	1.0253

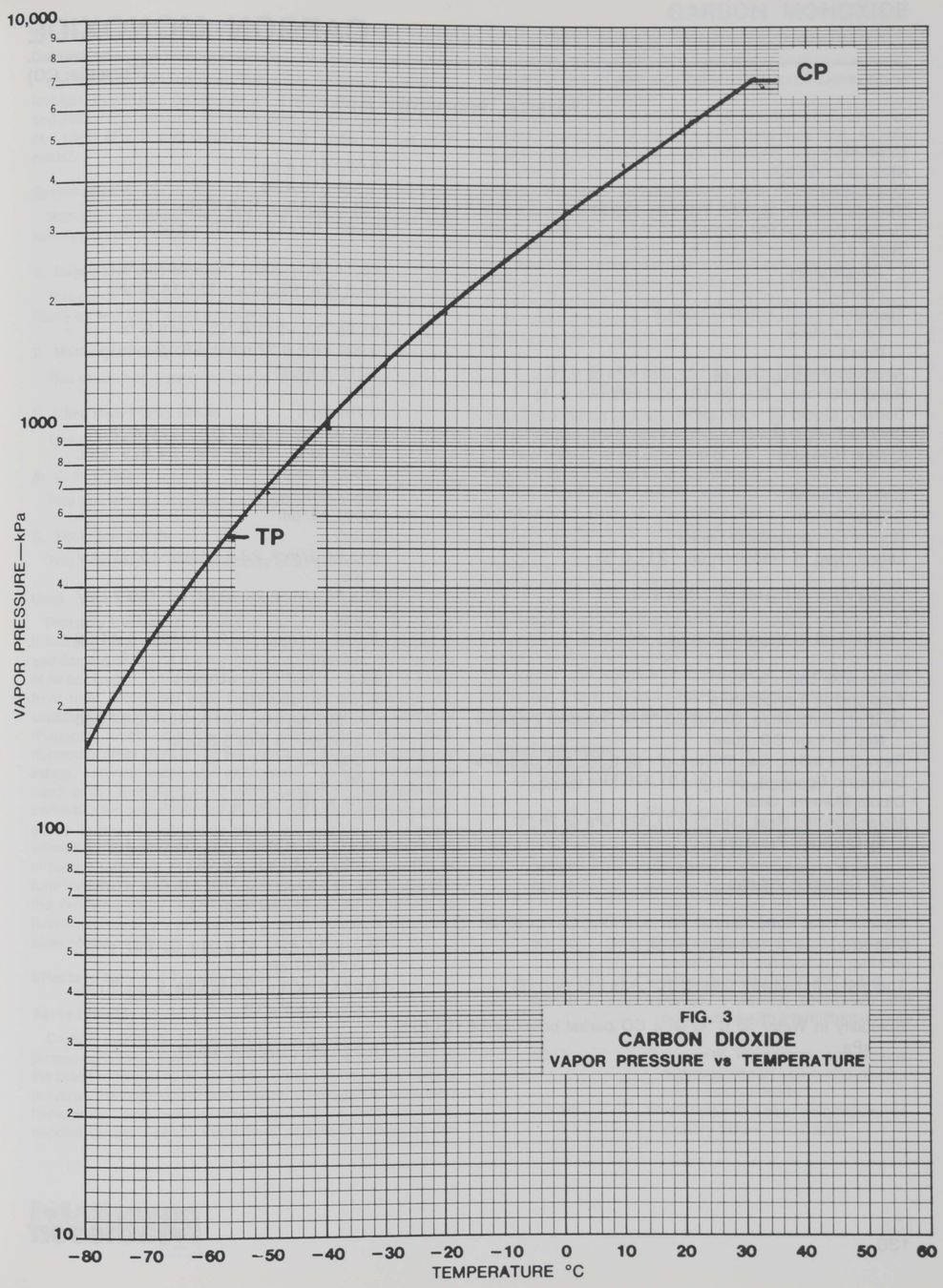


FIG. 3
CARBON DIOXIDE
VAPOR PRESSURE vs TEMPERATURE

CARBON MONOXIDE

(Formula: CO)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.028 010 4 kg
One Mole of CO	0.028 010 4 kg
Specific Volume @ 21.1 °C, 101.325 kPa	861.5 dm^3/kg; 13.8 ft^3/lb
Boiling Point @ 101.325 kPa	81.63 °K; −191.5 °C; −312.7 °F
Triple Point	
Temperature	68.14 °K; −205.1 °C; −337.0 °F
Pressure	15.3 kPa; 153 mbar; 115.14 mmHg
Transition Point, Solid I—Solid II	
Temperature	61.55 °K; −211.6 °C; −348.9 °F
Pressure	0.937 kPa; 9.37 mbar; 28.12 mmHg
Absolute Density, Gas @ 101.325 kPa @ 0 °C	1.250 4 kg/m^3
Relative Density, Gas @ 101.325 kPa (Air = 1)	0.967
Density, Liquid @ −191.5 °C	0.789 kg/l
Critical Temperature	132.92 °K; −140.2 °C; −220.4 °F
Critical Pressure	3 499 kPa; 34.99 bar; 34.529 atm; 507.4 psia
Critical Volume	3.322 dm^3/kg
Critical Density	0.301 kg/dm^3
Critical Compressibility Factor	0.295
Latent Heat of Transition @ −211.6 °C	633.04 J/mol; 22.6 kJ/kg; 151.3 cal/mol
Latent Heat of Fusion @ −205.1 °C	835.54 J/mol; 29.83 kJ/kg; 199.7 cal/mol
Latent Heat of Vaporization @ −191.5 °C	6.040 kJ/mol; 0.216 kJ/kg; 1 443.6 cal/mol
Flammable Limits In Air	12.5 − 74.2% (by volume)
Autoignition Temperature	925.2 °K; 652 °C; 1 206 °F
Heat of Combustion, Gas @ 25 °C at Constant Pressure	
Net, to form CO_2 (gas)	282.989 kJ/mol; 10.103 kJ/kg; 67.636 kcal/mol; 4 346.5 Btu/lb
Refractive Index, Gas White Light @ 0 °C, 101.325 kPa	1.000 340
Dielectric Constant, Gas @ 101.325 kPa @ 27 °C	1.002 9
Dipole Moment, Gas	3.74×10^{-30} C·m; 0.112 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	29.204 kJ/(kmol·°K); 29.204 J/(mol·°K); 1.043 kJ/(kg·°K)
@ Constant Volume	20.794 kJ/(kmol·°K); 20.794 J/(mol·°K); 0.742 kJ/(kg·°K)
Specific Heat Ratio, Gas @ 101.325 kPa, Cp/Cv @ 25 °C	1.404
Viscosity, Gas @ 101.325 kPa @ 0 °C	0.016 57 mPa·s; 0.016 57 $mN·s/m^2$; 0.016 57 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 0 °C	0.023 2 W/(m·°K); 55.49×10^{-6} cal·cm/(s·cm^2·°C)
Solubility in Water @ 0 °C @ a CO partial pressure of 101.325 kPa	3.537 cm^3/100 cm^3 water

Matheson

Description

Carbon monoxide is a toxic, flammable, colorless, and odorless gas. It is slightly lighter than air. It is shipped as a nonliquefied gas in high pressure steel cylinders at a maximum pressure of 11380 kPa (1 650 psig) at 21.1 °C, under special DOT permit.

Specifications

Matheson supplies five grades of carbon monoxide with specifications as follows:

1. Research Purity Grade

This grade is the highest purity and is available in Pyrex liter flasks as well as in small cylinders.

2. Matheson Purity Grade

This grade has a minimum purity of 99.99 mole %.

3. Ultra High Purity Grade

This grade has a minimum purity of 99.8 mole %.

4. C. P. Grade

This grade has a minimum purity of 99.5 mole %.

5. Technical Grade

This grade has a minimum purity of 99.0 mole %.

Uses

Probably the largest amount of carbon monoxide is utilized in fuel gas mixtures with hydrogen and other gases for industrial and domestic heating and for the reduction of ores. An example of its application is the Mond process for the recovery of nickel from ores containing iron, cobalt and copper. Smaller but substantial amounts are used in the manufacture of a variety of chemicals, such as acids, esters and alcohols, from which numerous other derivatives are manufactured, such as higher esters, ketones, aldehydes and glycols. Carbon monoxide is used in the manufacture of metal carbonyls (especially iron carbonyl) for conversion by thermal decomposition into powdered metals of high purity which are molded into complex articles by powder metallurgy. Carbon monoxide is also used in the manufacture of special catalysts by reacting metals to form carbonyls followed by decomposition of the carbonyls; the resulting metal catalysts are used in the synthesis of hydrocarbons or oxygenated compounds and in the hydrogenation of fats and oils.

Effects in Man and Toxicity (2)(3)

Acute Effects

Carbon monoxide is classified as a chemical asphyxiant, producing a toxic action by combining with the hemoglobin of the blood to form a relatively stable carboxyhemoglobin. It thus prevents the hemoglobin from taking up oxygen to form oxyhemoglobin, and consequently the body is deprived of its needed oxygen. Since the affinity of carbon monoxide for hemoglobin is about 200–300 times that of oxygen, only small amounts of carbon monoxide in the air will consequently cause toxic reactions to occur.

Carbon monoxide in excess of 50 ppm will produce symptoms of poisoning if breathed a sufficiently long time. As little as 200 ppm will produce slight symptoms (slight headache, discomfort) in several hours. A concentration of 400 ppm will produce headache and discomfort within two to three hours. With moderate exercise, 1 000–2 000 ppm will produce slight palpitation of the heart in 30 minutes, a tendency to stagger in 1½ hours, and confusion of the mind, headache, and nausea in 2 hours. A concentration of 2 000–2 500 ppm will usually produce unconsciousness in about 30 minutes. Its effects at higher concentrations may be so sudden that a man has little or no warning before he collapses. These effects are summarized in the following table (1):

Effect	Concentration (ppm)
Permissible for an exposure of 8 hours	50
Concentration which can be inhaled for 1 hour without appreciable effect	400–500
Concentration causing a just appreciable effect after 1 hour of exposure	600–700
Concentration causing unpleasant but not dangerous symptoms after 1 hour of exposure	1 000–2 000
Dangerous for exposure of 1 hour	1 500–2 000
Fatal in exposures of less than 1 hour	4 000 and above

The concentration, exposure time and physical activity of the individual will determine the percentage conversion of hemoglobin to carboxyhemoglobin. The effects produced depend on the degree and duration of saturation of blood with carbon monoxide. The symptoms caused by various amounts of carboxyhemoglobin in the blood are given in the following table:

Blood Saturation % Carboxyhemoglobin	Symptoms
0–10	No symptoms.
10–20	Tightness across forehead, possibly slight headache.
20–30	Headache and throbbing in temples.
30–40	Severe headache, weakness, dizziness, dimness of vision, nausea, vomiting, collapse.
40–50	Same as previous item but with more possibility of collapse and syncope, increased respiration and pulse.
50–60	Syncope, increased respiration and pulse, coma with intermittent convulsions.
60–70	Coma with intermittent convulsions, depressed heart action and respiration, possibly death.
70–80	Weak pulse and slow respiration, respiratory failure, and death.

Matheson

Chronic Effects

The effects of prolonged exposure to low concentrations of carbon monoxide are similar to the acute effects. Claims of permanent, harmful effects from prolonged exposure to low concentrations of carbon monoxide have been made, but they are not readily substantiated. There are several reports which indicate the absence of any signs of chronic carbon monoxide poisoning.

Carbon monoxide is a chemical asphyxiant and not a poison. Concentrations producing physiological effects are indicated in the above table. Carbon monoxide is not detectable by odor. The symptom of headache should be taken as a warning that a dangerous concentration is being inhaled.

The 1979 ACGIH has adopted a Threshold Limit Value (TLV) of 50 ppm (55 mg/m^3) for carbon monoxide (average concentration in air to which nearly all workers may be repeatedly exposed during an 8-hour day without harmful effects). The tentative Short Term Exposure Level (STEL) has been set at 400 ppm (440 mg/m^3).

First Aid Treatment (3) (4)

Remove the victim immediately to an uncontaminated atmosphere. If he is breathing, administer pure oxygen by the best method available (an oronasal mask is usually best). If breathing is weak or has stopped, start artificial respiration immediately and administer pure oxygen simultaneously (if it is readily available) but do not delay artificial respiration until a source of it is found.

Oxygen at greater than atmospheric pressure is more efficient as an antidote, the optimum range of pressures being 2 to 2.5 atm. A special mask or, preferrably, a compression chamber to utilize oxygen at these pressures, is required.

Medical Suggestions

Avoid stimulant drugs, including carbon dioxide. The addition of 5–7% carbon dioxide to oxygen, to serve as a respiratory stimulant, is a now regarded as more hazardous than beneficial. Do not inject methylene blue. Insure absolute rest in bed for at least 48 hours. Watch for late neurological and/or cardiac complications.

Precautions in Handling and Storage

The major hazards resulting from the handling of carbon monoxide stem from its extreme flammability and toxicity. This gas should, therefore, be handled in well-ventilated areas, preferably a hood. Systems carrying this gas should be thoroughly checked for leaks. The gas should never be handled in an area where the gas may diffuse to an open flame, excessive heat, or spark.

Do not store reserve stocks of carbon monoxide with cylinders containing oxygen, or other highly oxidizing or flammable materials. Carbon monoxide detectors should be installed in indoor areas when the gas is used regularly. Ground all lines and equipment used with carbon monoxide.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Equipment to contain carbon monoxide should be pretested for leaks with an inert gas (such as nitrogen). Leaks which may later develop during the actual operation may be detected by applying soap water to the suspected area; leaks will be indicated by bubble formation.

Analytical Detection

The concentration of carbon monoxide in the atmosphere can be determined with the Matheson-Kitagawa Toxic Gas Detector System Model 8014K. Detector tube numbers and measurable concentrations are shown below:

Model No.	Measurable Concentration (ppm)
100	10–1000 (NIOSH Certified)
106SA	10–100/100–1000
106SB	10–100/100–1000 (in the presence of ethylene)
106S	10–250 (NIOSH Certified)

Carbon monoxide can be determined quantitatively by means of an iodine pentoxide method (1) by a palladous chloride method (1) or by gas chromatography.

Materials of Construction

Corrosion by pure carbon monoxide at low pressures (less than 3 450 kPa (500 psig) can be considered negligible. However, any piping and vessels containing carbon monoxide should be adequately designed to meet ASME standards, and be approved by competent engineers.

At higher pressures, however, pure carbon monoxide will react with iron, nickel, and certain other metals forming carbonyls which are usually low boiling liquids or vapors. Pressure favors the reaction, and in the case of iron, it appears to be catalyzed by water vapor. Steel cylinders, in which the gas has been stored for long periods under pressure, may be found to contain quantities of iron carbonyl. The carbon monoxide may be freed from the carbonyl by passing it over activated charcoal or through a heated tube containing refractory material. The decomposition temperature of the iron carbonyl at 1 atm is about 180°C.

The presence of small amounts of sulfur compounds corrodes steel appreciably more than sulfur-free carbon monoxide. Only very highly alloyed chrome steels are sufficiently corrosion-resistant to carbon monoxide containing small amounts of sulfur-containing impurities (5). The book "Design of High Pressure Plant, and Properties of Fluid at High Pressure" by W. M. Newitt (6) states that iron and alloy steels are attacked by carbon monoxide; for this reason high pressure plant equipment for handling carbon monoxide is frequently lined with copper.

Matheson supplies all grades of carbon monoxide as sulfur-free material. It is strongly recommended, however, that corrosion tests be made with samples of materials of construction to determine if the high pressure use of carbon monoxide under actual conditions will be detrimental to the material chosen.

Cylinder and Valve Description

Carbon monoxide is packaged in DOT approved, high pressure steel cylinders, having a minimum service pressure of 12 410 kPa (1 800 psig). These cylinders may be filled to a

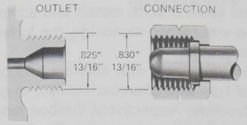


Fig. 1. **CONNECTION 350** .825"-14 LH EXT. accepting Round Shaped Nipple

maximum pressure of 11 380 kPa (1 650 psig). The cylinder valve outlet designated as the standard for carbon monoxide by the Compressed Gas Association (CGA) has a 0.825 inch left-hand external thread accepting a round-shaped nipple. It is designated as a standard No. 350 valve. Lecture bottles have a special 5/16 inch-32 threads per inch female valve outlet and 9/16 inch-18 threads per inch male dual valve outlet. Figure 1 shows a standard valve outlet and mating connection for carbon monoxide.

Safety Devices

Carbon monoxide safety devices are incorporated in the cylinder valve. The device consists of a frangible disc backed up with a fusible metal having a melting point of 100 °C (212 °F).

Recommended Controls

To reduce the high cylinder pressure of carbon monoxide to a safe working value consistent with a system's design, the following types of controls are recommended.

Automatic Pressure Regulators

1. Single Stage Regulators

A single stage regulator will reduce cylinder pressure in one single stage to a delivery pressure in a particular range, depending upon the design of the regulator and its spring load. A single stage regulator will show a slight variation in delivery pressure as cylinder pressure falls. The following Matheson single stage regulators are recommended for use with carbon monoxide:

Model No.	Delivery Pressure kPa	bar (g)	psig
1L-350	28–550	0.28–5.5	4–80
1H-350	69–1 240	0.69–12.4	10–180
2-350	340–4 480	3.4–44.8	50–650
3-350	690–10 340	6.9–103.4	100–1 500
3320 (for lecture bottles)	28–410	0.28–4.1	4.1–60

2. Two Stage Automatic Regulators

This type of regulator performs the same function as a single stage regulator. However, greater accuracy in control of delivery pressure is maintained and the delivery pressure does not vary as cylinder pressure falls. The following Matheson two stage regulators are recommended for use with carbon monoxide:

Model No.	Delivery Pressure Range kPa	bar (g)	psig
8L-350	14–104	0.14–1.04	2–15
8-50	28–340	0.28–3.4	4–50
8H-350	69–690	0.69–6.9	10–100
9-350	138–1720	1.38–17.2	20–250

3. Low Pressure Regulator

Accurate low pressure regulation of carbon monoxide can be obtained by using a Matheson Model 70 regulator in series with a Model 1L-350 regulator. The Model 70 regulator has an oversize, pancake body of die cast aluminum, a Buna N diaphragm, rubber seat, and a brass needle valve outlet, 1/4" NPT male, and hose connection. The delivery pressure range of this unit is 3.4–34.5 kPa (0.5–5.0 psig).

4. High Purity Regulators

Matheson single stage regulators Model 19-350 and Model 3500-350 are recommended for use with the Research Purity, Matheson Purity, and Ultra High Purity Grades of carbon monoxide.

The Model 19-350 regulator is constructed of brass and has a German silver alloy diaphragm (65% copper, 17% zinc, 18% nickel) plus a nylon seat and aluminum gaskets. The Model 19 regulator can be supplied with test results from helium leakage rate equipment. The regulator is provided with a diaphragm packless outlet valve (FF4373P) with 1/4" Gyrolok tube fitting. The Model 19 regulator has two 2½" gauges, a delivery pressure gauge 0–690 kPa (0–100 psig) and a cylinder pressure gauge of 0–20 680 kPa (0–3 000 psig). It has a delivery pressure range of 28–340 kPa (4–50 psig).

The Model 3500-350 stainless steel regulator has a body of 316 stainless steel, a 316 stainless steel diaphragm, a Tefzel® seat and Teflon gaskets. The Model 3500-350 has a delivery pressure range of 28–520 kPa (4–75 psig). It can be supplied with a helium leak rate certification, the maximum acceptable leak rate being 2×10^{-10} cm^3 per second inboard.

Two stage regulators Model 3800-350 and Model 3104-350, with delivery pressure ranges of 28–620 kPa and 28–690 kPa (4–100 psig), respectively, can be supplied for the same high purity grades.

Manual Controls

Manual needle valves for direct connection to the cylinder valve outlet are available. These types of controls are mainly used for intermittent flows or where it is desired to control the flow of gas directly from the cylinder, but these types of controls require close supervision. They should not be used as pressure controls, because dangerous pressures can develop if a line or system becomes plugged. Manual needle valves Model 50-350 or Model 52-350 with gauge to indicate tank pressure are recommended for use with carbon monoxide. These valves can be equipped with a serrated hose end, 1/4" compression fitting, or 1/4" NPT male or female outlets. The Model 30AR or Model 31B needle valve is recommended for use with lecture bottles of the C.P. and Technical Grades of carbon monoxide.

Manual control of high purity grades of carbon monoxide can be obtained with needle valve Model 4351-350.

Flowmeters

In all cases where accurate flow of a definite value must be known or reproduced, it is recommended that Matheson Series 7600 or 7200 brass flowmeter units be used.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Carbon monoxide is shipped in high pressure steel cylinders as a flammable compressed gas, taking a DOT "Red Gas Label". Cylinders are filled to a maximum of 10 340 kPa (1 500 psig) in accordance with present DOT regulations.

Commercial Preparations

Carbon monoxide can be prepared in a number of ways, as follows:

1. Carbon and oxygen combine at temperatures above 650 °C to form only the monoxide.
2. Carbon dioxide may be passed over hot coke. The dioxide is reduced to the monoxide.
3. Steam and hot coke will react to form carbon monoxide and hydrogen, in the water gas reaction.
4. Formic acid is dehydrated by sulfuric acid or phosphoric acid to yield carbon monoxide.
5. Carbon monoxide is obtained by decomposition of methyl formate using sodium methylate solution as a catalyst at about 60–100 °C.
6. Incomplete combustion of natural gas with oxygen or reforming with steam is commonly employed for the manufacture of commercial quantities of carbon monoxide.

Chemical Properties

Carbon monoxide is stable with respect to decomposition into carbon and oxygen. At 400–700 °C almost any surface is sufficiently active to cause disproportionation. Above 800 °C the equilibrium favors the formation of carbon monoxide. Carbon monoxide reacts reversibly with steam to give carbon dioxide and hydrogen.

At temperatures of 300–1500 °C, carbon monoxide reduces many metal oxides (like those of cobalt, copper, iron, lead, manganese, molybdenum, nickel, silver and tin) to lower metal oxides, metals, or metal carbides.

The alkali and alkaline earth metals and some of the heavy metals combine with carbon monoxide, the former giving salts and the latter carbonyls.

Carbon monoxide reacts with chlorine and bromine under the influence of light or a charcoal catalyst to give phosgene and carbonyl bromide, respectively. Carbon monoxide reacts slowly with liquid sulfur and rapidly with the vapor to give carbonyl sulfide. Aqueous bases absorb carbon monoxide forming formate salts.

Carbon monoxide reacts with Grignard reagents giving a variety of products—acyloins, alpha-diketones, and olefins being isolated.

Sodium alkyls react with carbon monoxide producing ketones, tertiary alcohols and other compounds.

Hydrogenation of carbon monoxide gives a variety of products, depending on the catalyst and conditions used: methane, benzene, paraffins, olefins, paraffin waxes, hydrocarbon high polymers, methanol, higher alcohols, ethylene glycol, glycerol and other oxygenated compounds being obtained.

Carbon monoxide adds to alcohols and, depending on the catalyst and conditions used, gives either formate esters or carboxylic acids and their esters.

Thermodynamic and Detailed Physical Data

Molecular Structure

The carbon monoxide molecule is considered to be a resonance hybrid involving the three structures depicted:

$$:\dot{C}:\ddot{O}:^{-} \qquad :C::\ddot{O}: \qquad :\bar{C}:::\dot{O}:^{+}$$

All three structures make about equal contributions to the normal state of the molecule.

The carbon monoxide molecule is stabilized by its very large resonance energy (58 kcal/mol).

The interatomic distance, 1.13 Å of :C::Ö: is compatible with the resonating structure. For $:\dot{C}:\ddot{O}:^{-}$ and $:\bar{C}:::\dot{O}:^{+}$, the interatomic distances are 1.25×10^{-10} m (1.25 Å) and 1.10×10^{-10} m (1.10 Å), respectively.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous carbon monoxide.

Vapor Pressure (7)

The vapor pressure of liquid carbon monoxide is represented by the following equation:

$$\log_{10} p = A - \frac{B}{t + C} \quad \text{or} \quad t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.69422, 291.743, and 267.996, respectively.

Some calculated vapor pressure values are shown below.

Matheson

Vapor Pressure

Temperature, °C	kPa	mbar	mmHg = torr
−203.43	20.00	200.0	150
−200.09	33.33	333.3	250
−196.70	53.33	533.3	400
−192.20	93.33	933.3	700
−191.49	101.325	1 013.25	760
−191.04	106.66	1 006.6	800
−189.02	133.32	1 333.2	1 000
−185.07	199.98	1 999.8	1 500

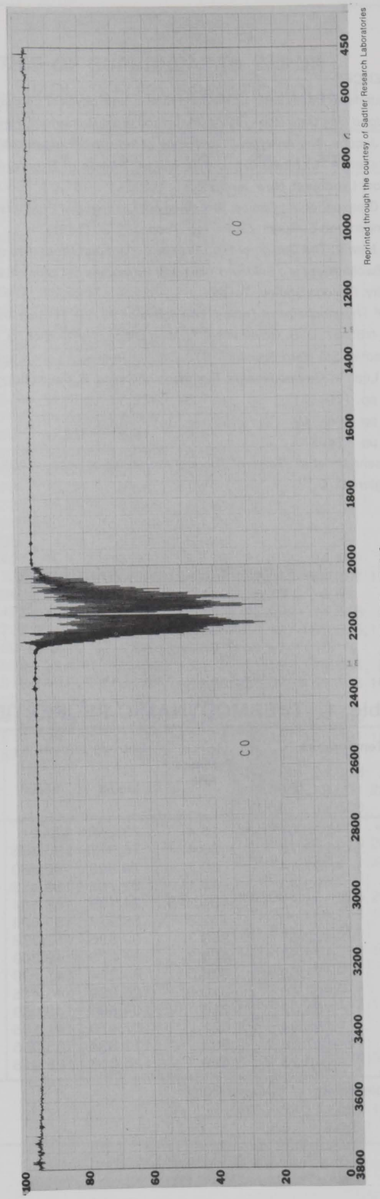
For additional vapor pressure data, see Table 1.

Thermodynamic Data

Thermodynamic properties of the saturated liquid and vapor are listed in Table 1, those for the superheated vapor in Table 2, and compressibility factors are shown in Table 3.

Thermodynamic Properties of Carbon Monoxide As Ideal Gas @ 25 °C (8)

Heat Capacity, C_p°	29.142 J/(mol·°K) 1.040 kJ/(kg·°K) 6.965 cal/(mol·°C)
Entropy, S°	197.543 J/(mol·°K) 7.052 kJ/(kg·°K) 47.214 cal/(mol·°C)
Free Energy Function, $(F^\circ_{298} - H^\circ_{298})/T$	−197.543 J/(mol·°K) −7.052 kJ/(kg·°K) −47.214 cal/(mol·°C)
Enthalpy, H°	8.669 kJ/mol 0.309 kJ/kg
Enthalpy of Formation, ΔH_f°	−110.529 kJ/mol −3.946 kJ/kg
Free Energy of Formation, ΔF_f°	−137.164 kJ/mol −4.897 kJ/kg



Reprinted through the courtesy of Sadtler Research Laboratories

© Sadtler 1972

Fig. 2. Infrared spectrum of gaseous carbon monoxide; 10 cm path length cell, with KBr windows; cell pressure: 26.66 kPa (200 mmHg) (9).

Matheson

REFERENCES

[1] For extensive tabulations of thermodynamic and physical properties of carbon monoxide, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1974*, Matheson, East Rutherford, New Jersey.

[2] M. B. Jacobs, *The Analytical Toxicology of Industrial Inorganic Poisons, 1967*, pp. 678–679, John Wiley & Sons, Inc., New York, New York.

[3] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Treatment*, 2nd edition, *1977*, pp. 24–29, Matheson, Lyndhurst, New Jersey.

[4] M. N. Gleason, *et al.*, *Clinical Toxicology of Commercial Products, 1969*, p. III–68, The Williams & Wilkins Company, Baltimore, Maryland.

[5] O. Sunden and E. Bohm, *Chem. Ing. Tech., 23*, 30 (1957).

[6] W. M. Newitt, *The Design of High Pressure Plant and Properties of Fluids at High Pressure, 1940*, p. 20, Claredon Press, Oxford, England.

[7] B. J. Zwolinski, *et al.*, Selected Values of Properties of Chemical Compounds, *1968*, Volume 1, Thermodynamic Research Center, Texas A & M University, College Station, Texas.

[8] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[9] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[10] A. S. Leah in *Thermodynamic Functions of Gases*, F. Din, editor, *1962*, Volume 1, p. 165, Butterworth Inc., Washington, D. C.

[11] **Ibid.**, pp. 170–171.

[12] **Ibid.**, pp. 168–169.

[13] **Ibid.**, pp. 174–175.

[14] J. Hilsenrath, *et al.*, *Table of Thermal Properties of Gases, 1955*, pp. 216–217, Natl. Bur. Stand. Circ. 564, U. S. Government Printing Office, Washington, D. C.

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED CARBON MONOXIDE (10)

Temperature		Pressure	Entropy J/(mol·°K)		Enthalpy kJ/mol		Latent Heat of Vaporization kJ/mol	Specific Volume dm^3/kg		Density kg/dm^3	
°K	°C	kPa	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
68.14*	−205.01*	15.4	73.358	170.21	3.400	9.993	6.593	1.182	1 277.7	0.846	0.000 783
72.42	−200.73	30.4	76.977	165.665	3.654	10.119	6.465	1.207	681.18	0.829	0.001 47
76.01	−197.14	50.7	79.898	162.469	3.871	10.147	6.276	1.232	431.98	0.812	0.002 32
79.72	−193.43	81.1	82.768	159.473	4.094	10.209	6.115	1.253	279.18	0.798	0.003 58
81.63	−191.52	101.325	84.199	158.164	4.210	10.246	6.036	1.267	227.06	0.789	0.004 40
85.36	−187.79	152.0	86.977	155.603	4.442	10.300	5.858	1.289	153.87	0.776	0.006 50
90.60	−182.55	253.3	90.525	152.323	4.754	10.352	5.598	1.328	95.286	0.753	0.010 50
96.11	−177.04	405.3	94.270	149.369	5.103	10.399	5.296	1.385	59.799	0.722	0.016 72
101.46	−171.69	608.0	98.224	147.139	5.494	10.457	4.963	1.439	40.414	0.695	0.024 74
105.69	−167.46	810.6	100.839	145.415	5.770	10.481	4.711	1.485	30.988	0.673	0.032 27
112.13	−161.02	1 216	104.684	143.059	6.183	10.486	4.303	1.582	20.707	0.632	0.048 29
117.21	−155.94	1 621	107.470	141.135	6.503	10.449	3.946	1.674	15.351	0.597	0.065 14
125.97	−147.18	2 533	113.834	136.055	7.337	10.137	2.800	1.939	8.533	0.516	0.117 20
132.92**	−140.23**	3 499	125.018	125.018	8.799	8.799	0.000	3.322	3.322	0.301	0.301

* Triple Point; **Critical Point

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED VAPOR

H, ENTHALPY, KJ/MOL (11); **S**, ENTROPY, J/(MOL·°K) (12); SPECIFIC VOLUME, DM^3/KG (13)

Pressure, kPa		Temperature, °C											
		−180	−140	−100	−50	−25	0	25	50	100	200	300	400
101.325	H	10.645	11.906	13.098	14.570	15.302	16.032	16.762	17.492	18.953			
	S	162.691	173.987	181.824	189.301	192.405	195.209	197.761	200.112	204.309			
	V	262.4	384.5	504.5	652.3	726.2	799.7	873.1	946.5	1 093			
506.6	H		11.699	12.969	14.06	15.252	15.994	16.731	17.464	18.932			
	S		159.327	167.887	175.715	178.883	181.736	184.314	186.673	190.887			
	V		73.11	98.86	129.7	144.6	159.4	174.4	189.2	218.8			
1 013.2	H		11.404	12.823	14.434	15.197	15.949	16.694	17.433	18.908			
	S		152.122	161.486	169.690	172.937	175.841	178.439	180.820	185.054			
	V		34.70	48/48	64/30	71.94	79.54	87.07	94.57	109.5			
2 533	H		10.598	12.500	14.262	15.064	15.839	16.598	17.349	18.843			
	S		139.917	152.523	161.507	164.912	167.887	170.540	172.954	177.247			
	V		10.67	18.17	25.12	28.37	31.56	34.69	37.81	43.95			
5 066	H		7.752	11.936	13.985	15.064	15.644	16.432	17.206	18.734			
	S		116.039	144.582	155.046	158.657	161.762	164.519	167.009	171.398			
	V		1.94	8.08	12.13	13.91	15.62	17.29	18.91	22.11			
10 132	H		7.500	10.730	13.651	14.328	15.211	16.064	16.899	18.527			
	S		112.027	133.645	147.147	151.239	154.624	157.611	160.297	164.979			
	V		1.67	3.30	5.82	6.83	7.78	8.68	9.56	11.25			
20 265	H			9.969	12.704	13.748	14.721	15.652	16.546	18.260			
	S			124.930	138.888	143.323	147.059	150.310	153.189	158.118			
	V			2.09	3.07	3.58	4.08	4.56	5.02	5.92			
30 398	H				12.438	13.529	14.427	15.477	16.391	18.139	21.505	24.793	28.015
	S				134.281	138.909	142.733	146.063	149.005	154.026	162.013	168.297	173.594
	V				2.36	2.67	2.99	3.30	3.61	4.21	5.38	6.51	7.60
40 530	H				12.401	13.479	14.478	15.432	16.353	18.123	21.992	24.856	28.203
	S				131.336	135.917	139.733	143.080	146.051	151.300	159.197	165.565	170.942
	V				2.05	2.27	2.50	2.72	2.95	3.39	4.27	5.13	5.96
50 662	H				12.473	13.546	14.539	15.486	16.403	18.172	21.592	24.954	28.337
	S				129.152	133.708	137.516	140.829	143.783	148.863	156.979	163.406	168.833
	V				1.88	2.05	2.22	2.39	2.57	2.92	3.62	4.31	4.98
101 325	H				13.374	14.428	15.410	16.341	17.242	18.985	22.389	25.809	29.308
	S				122.667	127.148	130.913	134.168	137.072	142.076	150.151	156.691	162.306
	V				1.50	1.59	1.67	1.75	1.83	2.00	2.34	2.68	3.01
101.325	H										20.420	24.888	27.950
	S										211.888	219.001	221.919
	V										1 387	1 680	1 973
506.6	H										21.885	24.881	27.950
	S										197.891	203.619	208.547
	V										277.8	336.6	395.4
1 013.2	H										21.872	24.874	27.950
	S										192.087	197.828	202.769
	V										139.2	168.7	198.2
2 533	H										21.834	24.855	27.950
	S										184.339	190.117	195.083
	V										56.1	68.0	79.9
5 066	H										21.724	24.811	27.955
	S										178.611	184.447	189.460
	V										28.3	34.4	40.4
10 132	H										21.679	24.796	27.962
	S										172.452	178.418	183.494
	V										14.5	17.7	20.7
20 265	H										21.556	24.771	28.012
	S										165.933	172.084	177.184
	V										7.64	9.28	10.9

Table 3. COMPRESSIBILITY FACTORS FOR CARBON MONOXIDE (14)

Temperature, °C	Pressure, kPa 101.325	405.3	709.3	1 013.2	4 053	7 093	10 133
−73	0.997 30	0.989 27	0.981 31	0.973 44			
−23	0.998 92	0.995 72	0.992 61	0.989 55	0.963 2		
27	0.999 66	0.998 66	0.997 72	0.996 83	0.990 7	0.989 6	0.993 5
127	1.000 23	1.000 95	1.001 69	1.002 45	1.011 3	1.022 5	1.035 9
227	1.000 40	1.001 63	1.002 86	1.004 11	1.017 2	1.031 4	1.046 9
327	1.000 45	1.001 80	1.003 16	1.004 53	1.018 6	1.033 2	1.048 5
427	1.000 45	1.001 80	1.003 16	1.004 52	1.018 3	1.032 5	1.047 0
527	1.000 43	1.001 74	1.003 04	1.004 35	1.017 5	1.030 9	1.044 5
627	1.000 41	1.001 65	1.002 88	1.004 12	1.016 6	1.029 1	1.041 8
727	1.000 39	1.001 55	1.002 71	1.003 88	1.015 6	1.027 3	1.039 1

CARBON TETRAFLUORIDE

(Synonyms: Tetrafluoromethane; Freon-14®)
(Formula: CF_4)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.088 005 kg
One Mole of CF_4	0.008 005 kg
Specific Volume @ 21.1 °C, 101.325 kPa	274.7 dm^3/kg; 4.4 ft^3/lb
Boiling Point @ 101.325 kPa	145.15 °K; −128.0 °C; −198.4 °F
Freezing Point @ 101.325 kPa	86.35 °K; −186.8 °C; −304.2 °F
Absolute Density, Gas @ 101.325 kPa @ 0 °C	3.946 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 0 °C (Air = 1)	3.05
Density, Liquid @ −80 °C	1.317 kg/l
Critical Temperature	227.59 °K; −45.6 °C; −50.0 °F
Critical Pressure	3 739 kPa; 37.4 bar; 36.9 atm; 542.3 psia
Critical Volume	1.590 dm^3/kg
Critical Density	0.629 kg/dm^3
Critical Compressibility Factor	0.276
Latent Heat of Fusion @ −186.8 °C	699.60 J/mol; 7.609 kJ/kg; 1.90 kcal/kg
Refractive Index, Liquid, n_D @ −73.3 °C	1.151
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	61.271 kJ/(kmol·°K); 61.271 J/(mol·°K); 0.696 kJ/(kg·°K); 0.166 4 kcal/(kg·°C)
@ Constant Volume	52.949 kJ/(kmol·°K); 52.949 J/(mol·°K); 0.602 kJ/(kg·°K); 0.143 8 kcal/(kg·°C)
Specific Heat Ratio, Gas @ 101.325 kPa, Cp/Cv @ 25 °C	1.157
Specific Heat, Liquid @ −100 °C	98.313 kJ/(kmol·°K); 98.313 J/(mol·°K); 1.117 kJ/(kg·°K); 0.267 kcal/(kg·°C)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.017 0 mPa·s; 0.017 0 $mN·s/m^2$; 0.017 0 cP
Viscosity, Liquid @ −60.0 °C	0.170 mPa; 0.170 $mN·s/m^2$; 0.170 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.017 99 W/(m·°K); 43.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −60.0 °C	0.071 96 W/(m·°K); 172 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −80.0 °C	6.4 mN/m; 6.4 dyn/cm
Dielectric Constant, Gas 24.5 °C, 50.7 kPa	1.000 6
Solubility In Water @ 25 °C, 101.325 kPa	0.001 5% (by weight)

Description

Carbon tetrafluoride is an inert, colorless, nonflammable gas. It is shipped by Matheson in steel cylinders as a nonliquified gas, in 1A cylinders at a pressure of 13 800 kPa (2 000 psig) at 21.1 °C, but in all other cylinders at a pressure of 3 447 kPa (500 psig) at 21.1 °C.

Specifications

Carbon tetrafluoride has a minimum purity of 99.7 mole %.

Uses

Carbon tetrafluoride is chiefly of interest as a low temperature refrigerant, and possibly as a gaseous insulator.

Effects In Man and Toxicity (2)

Inhalation of high concentrations of carbon tetrafluoride can cause such symptoms as dizziness, disorientation, incoordination, narcosis, nausea or vomiting. There appear to be no irreversible effects once the oxygen deficiency has been corrected. Carbon tetrafluoride does not have odor warning properties.

Skin contact with the liquid form of carbon tetrafluoride can cause skin irritation or frostbite.

Carbon tetrafluoride is relatively nontoxic according to the rating system devised by the Underwriters' Laboratories, Chicago, Illinois.

First Aid Treatment (2)

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration if needed and oxygen simultaneously. Treat symptomatically thereafter.

Skin Contact

In case of skin contact with liquid carbon tetrafluoride, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Leak Detection

Leaks of carbon tetrafluoride in lines and equipment may be detected by applying soap water solution to the suspected points. Leaks will be indicated by bubble formation. Also, the Matheson Leak Detector Model 8016 and 8017 are ideal for more sensitive detection of carbon tetrafluoride leaks.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-C.

Materials of Construction

Since carbon tetrafluoride is noncorrosive, common structural metals may be used. Systems should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

Carbon tetrafluoride is shipped in DOT approved, high pressure steel cylinders. Cylinders of carbon tetrafluoride are equipped with brass valves having Compressed Gas Association (CGA) cylinder valve outlet connection No. 320, the approved CGA alternate. The valve outlet has a thread size of 0.825 inch with right-hand external threads with a flat seat and using a washer as a seal (see Figure 1 for an illustration). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet and a 9/16 inch-18 threads per inch, male dual outlet.

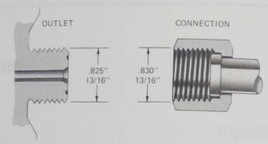


Fig. 1. CONNECTION 320 .825"-14 RH EXT. used with Flat Seat and Washer.

Safety Devices

Cylinders of carbon tetrafluoride have frangible discs as safety devices. They should, therefore, be stored away from sources of heat to prevent the development of pressures capable of rupturing the disc.

Recommended Controls

Automatic Pressure Regulators

In order to reduce the cylinder pressure of carbon tetrafluoride to a safe working pressure consistent with a system's design, the following automatic regulators are recommended for use.

1. Single Stage Regulators

A single stage regulator will reduce cylinder pressure in one stage to a delivery pressure in a particular range depending upon the design of the regulator and its spring load. A single stage regulator will show a slight variation in a delivery pressure as the cylinder pressure falls. The following single stage regulators are available from Matheson for use with carbon tetrafluoride.

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
1L-320	28–550	0.28–5.5	4–80
1H-320	69–1 240	0.69–12.4	10–180
2-320	340–4 480	3.4–44.8	50–650
3320 (for lecture bottles)	28–410	0.28–4.1	4–60

2. Two Stage Regulators

This type of regulator performs the same function as the single stage regulator. However, greater accuracy and control of delivery pressure is maintained, and the delivery pressure does not vary as cylinder pressure falls. The following two stage regulators are available from Matheson:

Matheson

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
8L-320	14–104	0.14–1.04	2–15
8-320	28–340	0.28–3.4	4–50
8H-320	69–690	0.69–6.9	10–100
9-320	138–1720	1.38–17.2	20–250

3. Low Pressure Regulator

For sensitive, accurate low pressure control, Matheson has available Model 70 regulators. These regulators have an aluminum body, an oversized Buna N rubber diaphragm, rubber seat and brass needle valve outlet, 1/4" NPT male, and hose connection. The Model 70 regulator is used in series with the Model 1L-320 regulator; inlet pressure must not exceed 1 724 kPa (250 psig). This combination will provide a delivery pressure range of 3.4–34.5 kPa (0.5–5.0 psig).

Manual Controls

Manual needle valve Model 50-320 or Model 52-320 with tank gauge, manufactured from brass bar stock, is available for direct connection to the cylinder valve outlet. Either valve may be equipped with a variety of outlets, such as a serrated hose end, 1/4" compression fitting, or 1/4" NPT male or female pipe. It should be used only where manual flow control is needed and should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. Needle valve Model 30AR or Model 31B is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 or 7200 laboratory brass flowmeter units are recommended for use where definite flow rates must be known.

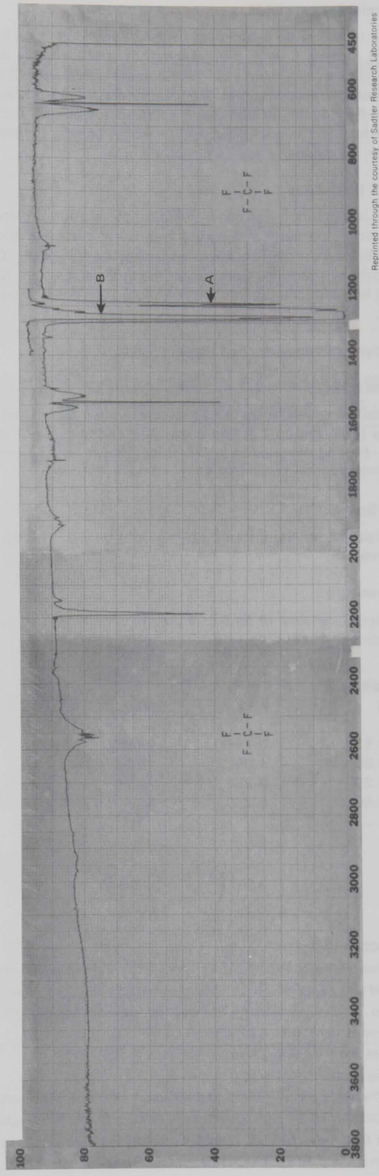
Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate reading are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Carbon tetrafluoride is classified by the DOT as a nonflammable compressed gas and is shipped with the required "Green Label".



Reprinted through the courtesy of Sadtler Research Laboratories
©Sadtler 1972

Fig. 2. Infrared spectrum of gaseous CF_4 in frequency range 3 800-450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure: curve A: 2.666 kPa (20 mmHg), curve B (partial scan): 0.066 7 kPa (0.5 mmHg) (7).

Matheson

Commercial Preparations

Carbon tetrafluoride is obtained by the direct fluorination of carbon in a metal tube in the presence of small amounts of mercury salts as explosion inhibitors. It is also obtained by an electrochemical process from acetic acid dissolved in liquid hydrogen fluoride. In the laboratory, it has been prepared from carborundum and fluorine, and from carbon dioxide, carbon monoxide, or phosgene and sulfur tetrafluoride.

Chemical Properties

Carbon tetrafluoride is extremely stable, reacting only slightly even at the temperature of a carbon arc. Carbon tetrafluoride reacts with carbon dioxide at temperatures above 1 000 °C giving carbonyl fluoride. Carbon tetrafluoride is resistant to oxidizing and reducing agents except under very drastic conditions.

Thermodynamic and Detailed Physical Data

Molecular Structure

The carbon tetrafluoride molecule has regular tetrahedral symmetry (point group T_d), and a symmetry number of 12. It has a C—F bond distance of 1.320×10^{-10} m (1.320 Å) and an F—C—F bond angle of 109.47°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous carbon tetrafluoride.

Vapor Pressure

The vapor pressure of liquid CF_4 up to slightly above the boiling point is shown below (3).

Temperature, °C	Vapor Pressure kPa	mbar	mmHg = torr
−180.65	0.200	2.000	1.5
−170.90	1.093	10.93	8.2
−163.29	3.266	32.66	24.5
−158.80	5.333	53.33	40.0
−155.40	7.999	79.99	60.0
−150.70	13.33	133.3	100.0
−143.60	26.66	266.6	200.0
−138.69	44.22	442.2	331.7
−133.19	68.97	689.7	517.3
−129.69	89.65	896.5	672.4
−127.98	101.5	1 015	761.4
−127.29	106.5	1 065	798.9

The vapor pressure up to the boiling point corresponds to the following equation (3):

$$\log_{10} p = 5.044\,20 - \frac{701.73}{T} + 1.75 \log_{10} T - 0.007\,671\,5T$$

in which p = mmHg and T = °K.

For additional vapor pressures below 760 mmHg and for vapor pressure data above 760 mmHg, see Table 1.

Latent Heat of Vaporization, ΔHv (4)
@ −128.0 °C 135.95 kJ/kg

For additional ΔHv values, see Table 1.

Thermodynamic Data

The thermodynamic properties of the saturated liquid and vapor and of the superheated vapor are listed in Table 1 and 2, respectively.

Thermodynamic Properties of Carbon Tetrafluoride As Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	61.053 J/(mol·°K)
Entropy, S°	261.308 J/(mol·°K)
Free Energy Function ($F_T^\circ - H_{298}^\circ)/T$	−261.308 J/(mol·°K)
Enthalpy, H°	12.732 kJ/mol
Enthalpy of Formation, ΔH_f°	−933.199 kJ/mol
Free Energy of Formation, ΔF_f°	−888.539 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of carbon tetrafluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, 1975, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure To Toxic Gases—First Aid and Medical Treatment*, 1977, 2nd edition, pp. 119-123, Matheson, Lyndhurst, New Jersey.

[3] W. Menzel and F. Mohry, *Z. Anorg. Chem. 210*, 257 (1933).

[4] E. G. King and K. K. Kelley, *Bur. Mines Bull. 592* (1961).

[5] *JANAF Thermochemical Tables*, 2nd edition, 1971, D. R. Stull and H. Prophet, project directors, Natl. Bur. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDA-NBS 37, U. S. Government Printing Office, Washington, D. C.

[6] *Freon-14 Bull. F-14, 1961*, E. I. duPont de Nemours & Co., Inc., Wilmington, Delaware.

[7] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED CARBON TETRAFLUORIDE (6)

Temperature, °C	Pressure kPa	bar	Entropy J/(mol·°K) Liquid	Vapor	Enthalpy kJ/mol Liquid	Vapor	Latent Heat of Vaporization kJ/mol	Specific Volume dm^3/kg Liquid	Vapor	Density kg/m^3 Liquid	Vapor
−145.56	23.9	0.239	130.789	230.317	8.608 8	21.308 4	12.699 6	0.579	499.5	1 726	2.001 8
−134.44	62.4	0.624	137.122	225.457	9.453 6	21.709 0	12.255 4	0.599	205.2	1 669	4.872 2
−123.33	139	1.39	143.382	221.701	10.364 2	22.096 4	11.732 2	0.622	97.52	1 607	10.255
−112.22	274	2.74	149.642	218.718	11.340 9	22.457 1	11.116 2	0.648	51.61	1 542	19.374
−101.11	489	4.89	155.865	216.251	12.386 9	22.775 8	10.388 9	0.679	29.60	1 472	33.781
−90.00	810	8.10	161.977	214.042	13.496 0	23.033 5	9.537 5	0.717	17.99	1 395	55.606
−78.89	1 260	12.6	168.052	211.980	14.668 6	23.201 1	8.532 5	0.765	11.34	1 308	88.212
−67.78	1 870	18.7	174.091	209.660	15.922 5	23.225 4	7.302 9	0.830	7.242	1 204	138.13
−56.67	2 680	26.8	180.572	206.531	17.346 7	22.969 7	5.623 0	0.937	4.483	1 067	222.13
−45.66	3 745	37.45	94.564	94.564	20.586 3	20.586 3	0.000	1.599	1.599	625.68	625.68

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED CF_4 VAPOR (6)

H, ENTHALPY, kJ/mol; **S**, ENTROPY, J/(mol·°K); **V**, SPECIFIC VOLUME, dm^3/kg

Pressure kPa		Temperature, °C −123.3	−73.3	−17.8	−37.8	93.8	143.9	260.0	371.1
101.325	H	22.135	24.441	27.383	30.709				
	S	224.499	237.755	250.679	262.462				
	V	135.4	183.8	236.6	289.0				
690	H		24.027	27.109	30.511				
	S		220.412	233.999	246.040				
	V		24.66	33.45	41.72				
1 380	H		23.417	26.766	30.274	34.070			
	S		212.496	227.261	239.670	250.900			
	V		10.63	15.91	20.43	24.69			
2 070	H			26.391	30.031	22.894			
	S			222.806	235.693	247.108			
	V			10.03	13.33	16.33			
3 450	H			25.516	29.529	33.544			
	S			215.957	230.170	242.063			
	V			5.244	7.654	9.652			
4 140	H			24.991	29.270	33.369	37.638	46.808	56.673
	S			212.790	227.997	240.148	250.974	270.231	287.022
	V			4.015	6.236	7.985	9.564	12.52	15.32
4 830	H	24.382	29.007	33.195	37.512	46.735	56.633		
	S	209.586	226.046	238.418	249.391	268.759	285.623		
	V	3.103	5.225	6.792	8.197	10.77	13.22		
6 890	H	22.384	28.203	32.684	37.144	46.527	56.515		
	S	200.161	221.001	234.257	245.598	265.297	282.309		
	V	1.610	3.421	4.663	5.730	7.642	9.414		

CARBONYL FLUORIDE

(Formula: COF_2)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.066 007 kg/kmol
One Mole of COF_2	0.066 007 kg
Specific Volume @ 21.1 °C, 101.325 kPa	355.8 dm^3/kg; 5.7 ft^3/lb
Vapor Pressure @ 21.1 °C	5 620 kPa; 56.2 bar 814.7 psia; 55.44 atm
Boiling Point @ 101.325 kPa	188.58 °K; -84.6 °C -120.2 °F
Triple Point	
Temperature	161.89 °K; -111.3 °C; -168.3 °F
Pressure	12.52 kPa; 125 mbar; 93.9 mmHg
Absolute Density, Gas @ 101.325 kPa @ 20 °C	2.764 kg/m^3
Relative Density, Gas @ 101.325 kPa (Air = 1) @ 20 °C	2.29
Density, Liquid @ -114 °C	1.139 kg/l
Critical Properties calculated as described by Reid and Sherwood (2)	
Critical Temperature	295.95 °K; 22.8 °C 73.0 °F
Critical Pressure	5 760 kPa; 57.6 bar; 56.8 atm; 834.7 psia
Critical Volume	1.821 dm^3/kg
Critical Density	0.549 kg/dm^3
Critical Compressibility Factor	0.281
Latent Heat of Fusion @ -111.3 °C	24 300 J/kg; 24.3 kJ/kg; 5.8 kcal/kg
Latent Heat of Vaporization @ -84.6 °C	66 220 J/kg; 66.2 kJ/kg; 15.8 kcal/kg
Dipole Moment	3.17×10^{-30} C·m; 0.951 D
Molar Specific Heat, Liquid @ -85.2 °C	108.5 kJ/(kmol·K); 108.5 J/(mol·°K); 25.9 cal/(mol·°C)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.017 3 mPa·s; 0.017 3 $mN·s/m^2$; 0.017 3 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.0153 6 W/(m·°K); 37×10^{-6} cal·cm/(s·cm^2·°C)

Description

Carbonyl fluoride is a colorless, pungent, toxic gas. It is shipped as a liquefied gas under its own vapor pressure of 5516 kPa (800 psig) at 21.1 °C.

Specifications

Carbonyl fluoride has a minimum purity of 97%.

Uses

Carbonyl fluoride is an important intermediate for the preparation of organic fluorine compounds.

Effects in Man and Toxicity (3)

The 1979 ACGIH has established a Threshold Limit Value (TLV) of 5 ppm (15 mg/m^3) for carbonyl fluoride.* The concentration that produces acute effects varies with the time of exposure; 50 ppm may be fatal if inhaled for 30–60 minutes. Less severe exposures cause irritation of the nose and eyes, smarting of the skin, some degree of conjunctival and respiratory irritation. More severe exposures can lead to severe irritation of the eyes and eyelids and to inflammation and congestion of the lungs and circulatory (cardiovascular) collapse. Skin contact with the liquid or vapor can cause severe burns.

Carbonyl fluoride is readily detectable in air by its sharp, irritating odor.

The LC_{50} of carbonyl fluoride in the rat by inhalation is 360 ppm/1 hour.

* 1979 ACGIH Notice of Intent to Change to 2 ppm (5 mg/m^3).

First Aid Treatment

Speed in removing the patient from the contaminated atmosphere or removing the vapor or liquid from the skin or eyes is essential. First aid must be started immediately in all cases of contact with the gas in any form. All affected persons should

be referred to a physician, no matter how slight the injury, and the physician given a detailed account of the accident.

Inhalation

In minor exposures, remove the victim to an uncontaminated atmosphere and administer as quickly as possible 100% oxygen. It has been found helpful to expose even borderline cases to 100% oxygen at half hour intervals for 3-4 hours. In severe exposures, the worker must be carried at once into an uncontaminated atmosphere. A physician should be called immediately and the administration of 100% oxygen should be started at once. The victim should receive oxygen under positive pressure (<4 cm) for half hour periods for at least 6 hours until breathing is easy and the color of the skin and mucous membranes is normal. He should be kept comfortably warm, but not hot. Under no circumstances should the patient be permitted to return home or to work following a severe exposure until examined and discharged by a physician who is aware of the nature of the exposure. Mild analgesics and sedatives (such as aspirin or sodium bromide) may be given if thought to be desirable by the physician, but medication is usually unnecessary when adequate oxygen has been administered immediately after exposure. Morphine and barbiturates should never be given because of their depressant effect on respiration. Cardiac and respiratory stimulants are not recommended.

Artificial respiration should not be given unless breathing has ceased.

Contact with Eyes

If the eyes have been contacted by carbonyl fluoride, they should be flushed with water for at least 15 minutes. This may have to be repeated several times. Ice compresses should be applied when not irritating. Pain can be relieved by 2 or 3 drops of 0.5% tetracaine (pontocaine). An ophthalmologist should be consulted for more definite treatment. Ophthalmologists may be interested in a method of treatment for chemical burns of the eye described by R. S. McLaughlin in the American Journal of Ophthalmology, 29: 1355 (1946).

Contact with Skin

Workers who have had skin contact with carbonyl fluoride should be subjected to a drenching shower of water. The clothing should be removed as rapidly as possible while the victim is in the shower, and medical assistance obtained immediately. It is essential that the affected area be washed with copious quantities of water for a sufficient period of time to remove all acid from the skin. Following this an iced aqueous or alcohloic solution of 0.13% (1:750) of benzalkonium chloride, an iced 70% alcohol solution or an ice cold saturated solution of magnesium sulfate (Epsom salt) should be applied to the affected part for at least 30 minutes. If the burn is in such an area that it is impractical to immerse the part, then the iced solution should be applied with saturated compresses, which should be changed at least every two minutes. The physician should be available by then to administer further treatment before the completion of the iced solution treatment. If, however, a physician is not available by that time, the treatment with one of the iced solutions should be continued for 2-4 hours. It is then permissible to apply a generous quantity of paste made from powdered magnesium oxide and glycerine, freshly prepared. The paste is prepared by adding U. S. P. glycerine to U. S. P. magnesium oxide to form a thick paste. This paste should be applied daily for several days. Oils and greases should not be applied except under order by a physician.

The development of severe burns has also been prevented by infiltrating the skin and subcutaneous tissues with 10% calcium gluconate solution along with a local anesthetic.

Precautions in Handling and Storage

1. Employees should be instructed in appropriate handling and safety procedures and to avoid contact with carbonyl fluoride at all times.
2. Adequate emergency showers and wash-up facilities should be available in areas where carbonyl fluoride is used.
3. Eye-wash fountains should be placed in accessible locations and workers instructed in their use.
4. A hose mask, air-line mask or a self-contained breathing apparatus should be conveniently located in case of emergency, but in areas less likely to become contaminated.
5. Workers handling carbonyl fluoride should use full coverage of clothing at all times: rubber shoes soled with neoprene or an equally resistant material, or rubbers made of the same materials; a hat or protective head covering; a full mask and/or chemical goggles with plastic lenses; gauntlet-type gloves made of neoprene, plasticized polyvinyl chloride (0.028 inch thick) or an equally resistant material.
6. Leaking cylinders should be removed to the outdoors or to an isolated, well-ventilated area, and the contents transferred to other suitable containers or disposed of in a safe manner.
7. All spillage should be flushed promptly with water. Excessive quantities of carbonyl fluoride should be neutralized with soda ash or lime before admitting wastes to drains and sewers.
8. Waste disposal of carbonyl fluoride and materials containing it depends to a great extent upon local conditions. All local, state and federal regulations regarding health and pollution must be followed.
9. When carbonyl fluoride is discharged from the cylinder into liquids, the delivery tube should not extend below the surface of the liquid without the proper safeguards to prevent suckback. A check valve or trap should be inserted between the liquid and the cylinder. If suckback into the cylinder occurs, dangerous pressures may be formed within the cylinder.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Equipment to contain carbonyl fluoride should be pretested for leaks with *dry* compressed air or an inert gas like nitrogen. Leaks of carbonyl fluoride will be self evident since it fumes in moist air. Small leaks of carbonyl fluoride may be detected by holding an open bottle of concentrated aqueous ammonia near the suspected site of the leak. Leaks at the cylinder valve may be eliminated by tightening the stem, packing nut, or outlet cap. If a cylinder leak is such that it cannot be stopped by ordinary methods, call the supplier immediately; meanwhile, the cylinder should be removed from the storage or use area

and exhausted into a caustic absorption system following the disposal procedure described in Appendix II-D.

Materials of Construction

Carbonyl fluoride when used in anhydrous equipment with anhydrous reagents is not corrosive to ordinary metals. In the presence of moisture, however, corrosive conditions will develop rapidly, in which case copper, monel or nickel reactors and lines may be used. Piping and vessels to contain carbonyl fluoride should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

Carbonyl fluoride is shipped DOT approved, high pressure, steel cylinders equipped with valves having the Compressed Gas Association (CGA) cylinder valve outlet No. 660, the approved alternate standard. The valve has a thread size of 26.16 mm (1.030 inches) with right-hand external threads with

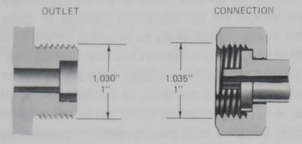


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

a flat seat and using a Teflon washer as a seal (see Figure 1 for an illustration of this valve outlet and its mating connection).

Safety Devices

No safety devices are permitted to be used on cylinders of carbonyl fluoride.

Recommended Controls

Automatic Pressure Regulator

Matheson supplies a single stage regulator designated as Model B15-660 for use with carbonyl fluoride. This regulator will deliver from 28-340 kPa (4-50 psig). It has a single gauge indicating delivery pressure only. The regulator is brass chemically coated with nickel and has internal parts of monel. The diaphragm is Kel-F backed with silver-plated nickel-silver alloy, the seat is Kel-F and the gasket is Teflon. The needle valve on the outlet is monel. A monel check valve Model 402V is recommended for use with this regulator to prevent suckback of foreign materials into the regulators.

Manual Controls

For manual flow control, Matheson has available a monel needle valve Model 55A-660, for direct connection to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, ¼" compression fitting, or ¼" NPT male or female pipe. The valve is suitable for intermittent flow control, but does not control pressure. Thus, it will not prevent pressure from building up if the system becomes clogged or if the system itself is closed.

Flowmeters

Matheson Series 7600 laboratory monel flowmeter units with 150 mm tubes and floats are recommended for use where definite flow rates must be known.

Shipping Regulations

Carbonyl fluoride is classified as a "Class A" poison and is shipped under the Dot required "Poison Gas Label".

Chemical Preparation

Carbonyl fluoride is prepared by fluorination of phosgene with sodium fluoride in acetonitrile, by fluorination of phosgene with a mixture of antimony trifluoride and antimony pentafluoride, or by fluorination of carbon monoxide by silver(II) fluoride.

Chemical Properties

Carbonyl fluoride fluorinates carbonyl compounds; thus, cyclohexanone and benzophenone give gem-difluorides. It reacts with perfluoroolefins in the presence of a metal fluoride to give perfluoroacyl fluorides. It reacts with alcohols and amines to give esters and amides, respectively, of fluorocarbonic acid, and with trifluoromethyl hypofluorite at 250-300 °C to give perfluorodimethyl peroxide. Carbonyl fluoride is hydrolyzed rapidly by water to give carbon dioxide and hydrogen fluoride.

Thermodynamic and Detailed Physical Data

Molecular Structure

The planar COF_2 molecule has C_{2v} symmetry and a symmetry number of two. The C—F and C=O bond distances are 1.312×10^{-10} m and 1.174×10^{-10} m, respectively. The F-C-F bond angle is 108 ° and the F-C-O bond angle is 126.02 °.

Infrared Spectrum

See Figures 2, 3, and 4 for the infrared spectrum of gaseous carbonyl fluoride.

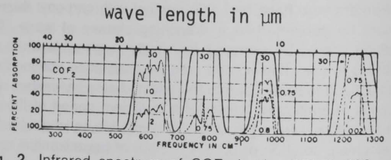


Fig. 2. Infrared spectrum of COF_2 in the 250-1 300-cm^{-1} region (6).

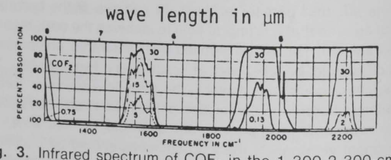


Fig. 3. Infrared spectrum of COF_2 in the 1 300-2 300-cm^{-1} region (6).

Matheson

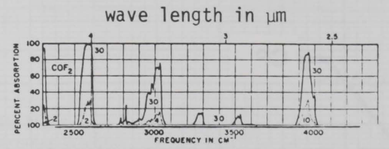


Fig. 4. Infrared spectrum of COF_2 in the 2 300-4 200-cm^{-1} region (6). The cells used for the above infrared absorption measurements were of fluorothene, and 10 cm long. Windows of NaCl, KBr, AgCl, and KRS-5 were used, in the appropriate regions. Pressures are as indicated, in inHg.

Vapor Pressure

The vapor pressure of liquid carbonyl fluoride from −111.3 °C to −84.0 °C is shown below. (Also, see Figure 5).

	Vapor Pressure		
Temperature, °C	kPa	mbar	mmHg = torr
−111.3	12.52	125.2	93.9
−109.6	14.61	146.1	109.6
−104.2	23.81	238.1	178.6
−98.2	38.65	386.5	289.9
−93.7	54.21	542.1	406.6
−90.3	69.35	693.5	520.2
−87.4	84.16	841.5	631.2
−85.0	99.00	990.1	742.6
−84.6	101.325	1 013.25	760.0
−84.0	105.16	1 051.5	788.7

The vapor pressure of liquid COF_2, from the triple point (−111.3 °C) to its normal boiling point (−84.6 °C) is represented by the following equation (4):

$$\log_{10} p = 31.086\,907 - \frac{1\,682.174\,8}{T} - 8.475\,432 \log_{10} T$$

in which p = mmHg and T = °K.

The vapor pressure of solid COF_2 from −143.2 °C to −111.3 °C is represented by the following equation (4):

$$\log_{10} p = 80.946\,550 - \frac{3\,017.133\,8}{T} - 27.311\,382 \log_{10} T$$

in which p= mmHg and T= °K.

Thermodynamic Properties of Carbonyl Fluoride as Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	47.254 J/(mol·°K)
	0.716 kJ/(kg·°K)
Entropy, S°	258.784 J/(mol·°K)
	3.921 kJ/(kg·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/T$	−258.784 J/(mol·°K)
	−3.921 kJ/(kg·°K)
Enthalpy, H°	−11.117 kJ/mol
	−168.4 kJ/kg
Enthalpy of Formation, ΔH_f°	−638.897 kJ/mol
	−9.679.2 kJ/kg
Free Energy of Formation ΔF_f°	−623.357 kJ/mol
	−9 443.8 kJ/kg

REFERENCES

[1] For extensive tabulations of thermodynamic and physical properties of carbonyl fluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, 1975, Matheson, East Rutherford, New Jersey.

[2] R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids*, 2nd edition, *1966*, pp. 6-44, McGraw-Hill Book Co., Inc., New York, New York.

[3] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases-First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 83-87, Matheson, Lyndhurst, New Jersey.

[4] E. L. Pace and M. A. Reno, *J. Chem. Phys.* 48, 1231-1235 (1968).

[5] JANAF Thermochemical Tables, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[6] A. H. Nielsen, *et al.*, *J. Chem. Phys. 20*, 596-604 (1952).

Matheson

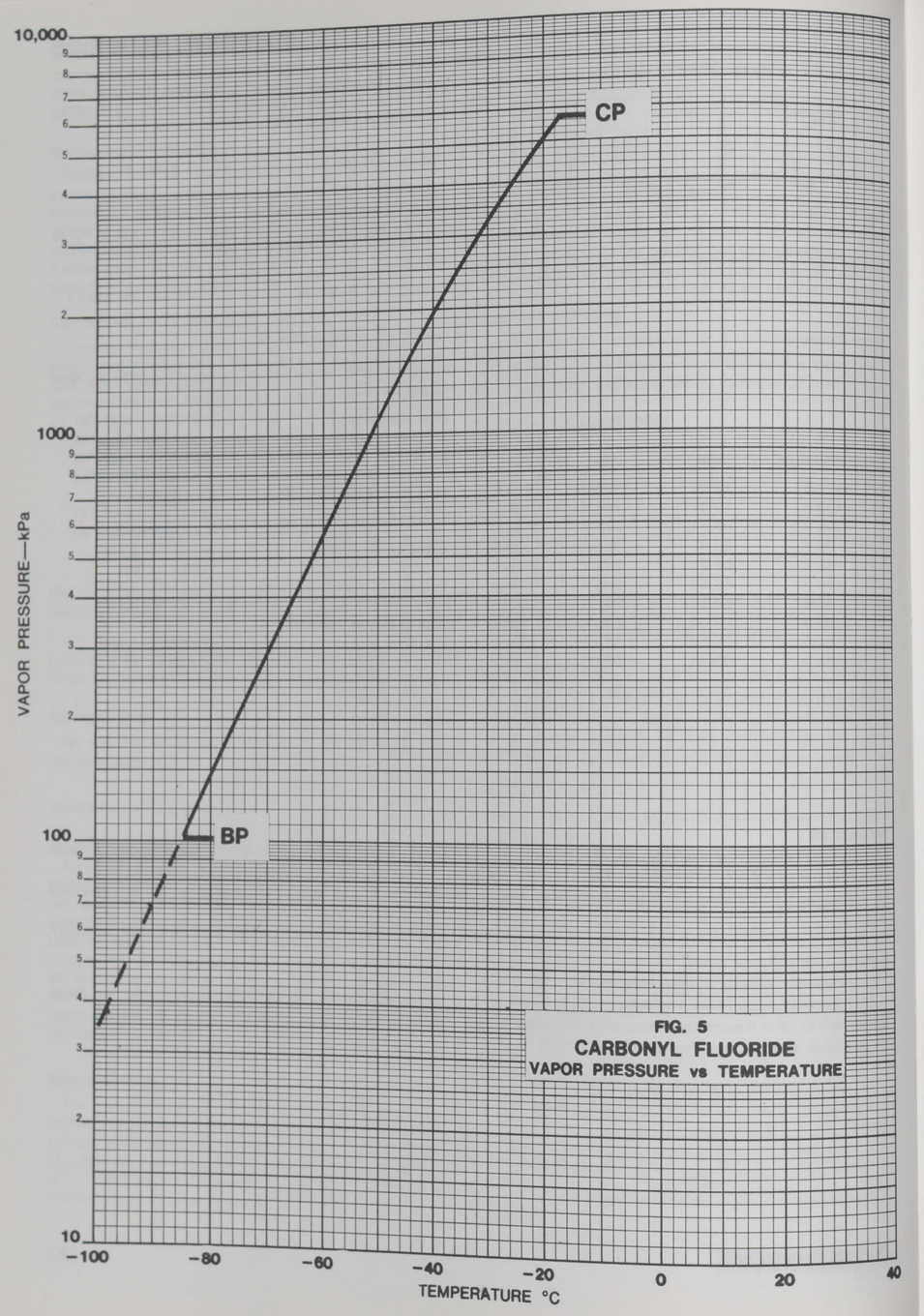


FIG. 5
CARBONYL FLUORIDE
VAPOR PRESSURE vs TEMPERATURE

CARBONYL SULFIDE

(Synonym: Carbon Oxysulfide)
(Formula: COS)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.060 070 kg
One Mole of COS	0.060 070 kg
Specific Volume @ 21.1 °C, 101.325 kPa	402.0 dm^3/kg; 6.44 ft^3/lb
Vapor Pressure @ 21.1 °C	1 204.5 kPa; 12.05 bar; 174.7 psia; 11.89 atm
Boiling Point @ 101.325 kPa	223.0 °K; 50.2 °C; -58.3 °F
Triple Point	
Temperature	134.30 °K; -138.8 °C; -217.9 °F
Pressure	0.101 325 kPa; 1.013 25 mbar; 0.760 mmHg
Absolute Density, Gas @ 101.325 kPa @ 20 °C	2.527 kg/m^3
Relative Density, Gas @ 101.325 kPa (Air = 1) @ 20 °C	2.10
Density, Liquid @ Saturation Pressure @ -80 °C	1.238 kg/l
Critical Temperature	375.15 °K; 102.0 °C; 215.6 °F
Critical Pressure	5 877 kPa; 58.77 bar; 58.0 atm; 852.4 psia
Critical Volume	2.331 dm^3/kg
Critical Density	0.44 kg/dm^3
Critical Compressibility Factor	0.264
Latent Heat of Fusion @ -138.8 °C	78 660 J/kg; 78.66 kJ/kg; 18.80 kcal/kg
Flammable Limits in Air	12–29% (by volume)
Dipole Moment	2.385×10^{-30} C·m; 0.715 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	42.752 kJ/(kmol·°K); 42.752 J/(mol·°K); 10.218 cal/(mol·°C)
@ Constant Volume	34.438 kJ/(kmol·°K); 34.438 J/(mol·°K); 8.209 cal/(mol·°C)
Specific Heat Ratio, Gas @ 101.325 kPa, Cp/Cv @ 25 °C	1.241
Viscosity, Gas @ 101.325 kPa @ 0 °C	0.011 66 mPa; 0.011 66 $mN·s/m^2$; 0.011 66 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.010 88 W/(m·°K): 26×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ -69.5 °C	24.06 mN/m; 24.06 dyn/cm
Solubility in Water @ 101.325 kPa @ 0 °C	1.333 cm^3/1 cm^3 water

Description

Carbonyl sulfide is a colorless, flammable, toxic gas, having an unpleasant odor similar to rotten eggs. It is shipped as a liquefied gas under its own vapor pressure of 1103 kPa (160 psig) at 21.1 °C.

Specifications

Matheson carbonyl sulfide has a minimum purity of 97.5 mole %.

Uses

Carbonyl sulfide is particularly useful in the synthesis of thioacids, S-trisubstituted carbinols, substituted thiazoles and substituted thiocarbamic acids (salts). High yields are obtained in the synthesis of substituted thiazoles.

Effects in Man (2)

Carbonyl sulfide is only slightly irritating to the lungs. It acts principally on the central nervous system, with death resulting

mainly from respiratory paralysis. Rabbits showed some ill effects after ½ hour exposure to 1 300 ppm, convulsions and death following an exposure of 1 hour to 3 200 ppm, 90 seconds to 2 900 ppm and 35 minutes to 1 200 ppm. Sixteen minutes exposure to 900 ppm caused no perceptible effects.

Experience with exposure of human beings has not been recorded. It is probable that the effects can be assigned to the action of hydrogen sulfide resulting from partial decomposition in the lungs and after absorption into the blood stream.

Toxicity

Toxic exposures are indicated in the above section. Carbonyl sulfide is considered to be a general poison in that it shows both mild irritant effects and systemic poisoning. Symptoms such as headache, giddiness, vertigo, and confusion should be taken as a warning that a dangerous concentration is being inhaled. The disagreeable odor of carbonyl sulfide is not considered to be a reliable warning property because of the likelihood of olfactory fatigue.

First Aid Treatment

Inhalation

Remove the victim to an uncontaminated atmosphere. Keep him warm and at rest. If he is breathing and conscious, recovery is expected to be rapid. If breathing is weak or has ceased, give artificial respiration and oxygen at once. Give oxygen until completely recovered. Otherwise treatment is symptomatic and supportive.

Contact with Eyes

Irrigate eyes with water for at least 15 minutes. Conjunctivitis may be relieved by instilling 1 drop of olive oil in each eye and sometimes by 3 or 4 drops of epinephrine sulfate (1:1 000) at frequent intervals (e.g., 5 minutes). Occasionally local anesthetics and hot and cold compresses are necessary to control the pain. Take victim promptly to an eye specialist for definite treatment.

Contact with Mucous Membranes of Nose

Flush with water for at least 15 minutes.

Precautions in Handling and Storage

Since carbonyl sulfide does not adequately warn the user of its presence, it should be stored and used in a well-ventilated area (preferably a hood) away from any sources of heat, sparks or open flames. Never use flames to detect flammable gas leaks; use soap water solution. Do not use carbonyl sulfide around sparking motors or other non-explosive-proof equipment. Do not store reserve stocks of carbonyl sulfide cylinders with cylinders containing oxygen, chlorine or other highly oxidizing or flammable materials. A check valve or trap of adequate size to take the total volume of the liquid should be used to prevent suckback of materials into the cylinder.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Never use a flame to detect carbonyl sulfide leaks; use soap water solution. Leaks will be evident by the formation of bubbles. If a leak appears around the cylinder valve stem, the valve packing nut should be tightened. If leaks persist, do not attempt to fix them without first contacting the supplier. Remove the cylinder to an isolated area (preferably a hood) or out-of-doors where the gas can be safely bled off.

Analytical Detection

Methods for the quantitative determination of carbonyl sulfide have been described (see Reference 3).

Disposal of Leaking Cylinders

Put on appropriate gas mask and transport the leaking cylinder to a safe out-of-doors area. Post warnings to prevent persons from approaching the cylinder with lit cigarettes or open flames or sparks. Proceed with disposal of the gas as described in Appendix II-D, using alcoholic potassium hydroxide or alkaline hypobromite as the absorbing solution.

Carbonyl sulfide can also be disposed of by burning.

Materials of Construction

Since carbonyl sulfide is noncorrosive no special materials of construction are required, provided the system is dry. Moisture will slowly decompose carbonyl sulfide into carbon dioxide and hydrogen sulfide which will create corrosion problems, requiring the use of stainless steel or aluminum. Piping or vessels should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

Carbonyl sulfide is shipped in DOT approved cylinders. Matheson uses the standard hydrogen sulfide valve outlet for carbonyl sulfide service. It is designated as Compressed Gas Association (CGA) No. 330, and is 0.825 inches in diameter, with left-hand external threads, with a flat seat and washer. Figure 1 illustrates the valve outlet and mating connection.

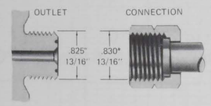


Fig. 1. CONNECTION 330 .825"-14 LH EXT. used with Flat Seat and Washer

Lecture bottles are equipped with a 5/16"-32 threads per inch female valve outlet.

Safety Devices

Cylinders of carbonyl sulfide have a safety device of fusible metal, melting at approximately 73.9 °C (165 °F). Cylinders over 76.2 cm (30 inches) long require this device in both ends of the cylinder.

Matheson

Recommended Controls

Automatic Pressure Regulator

Single stage regulator Model 11-330 is recommended for use with carbonyl sulfide cylinders. The regulator is constructed of an anodized aluminum body with type 316 stainless steel internal parts, plus a diaphragm of FEP Teflon on Viton and a Kel-F seat. No cylinder pressure gauge is necessary since it would not indicate cylinder content but only vapor pressure, which will remain constant as long as any liquid remains in the cylinder. Cylinder content should be determined by weighing. The delivery pressure range of this regulator is 28-550 kPa (4-80 psig).

Sensitive, and accurate control at low pressures can be obtained with Model 71 low pressure regulators. These regulators have oversized pancake bodies of aluminum with type 303 stainless steel internal parts, and Teflon seats. The Model 71 and Model 71A have Teflon coated Butyl rubber diaphragms. The delivery pressure range of Models 71 and 71A are 3.4–55 kPa (0.5-8 psig) and 34.5–83 kPa (5-12 psig), respectively.

To prevent suckback of foreign materials into a regulator, a stainless steel check valve is recommended for use with either of the above regulators.

Manual Controls

Series 61-330 stainless steel needle valves are recommended for use with carbonyl sulfide. This type of valve may be equipped with a variety of outlets, such as a hose connection, ¼" tube fitting or ¼" NPT male or female pipe. This type of valve is suitable for intermittent flow control but does not control pressure. Thus, it will not prevent pressure from building up if the system becomes clogged or if the system itself is closed.

Stainless steel needle valve Model 32S or Model 59 is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Carbonyl sulfide is shipped in low pressure steel cylinders as a flammable, compressed gas, taking a DOT "Red Gas Label".

Chemical Preparation

Carbonyl sulfide may be obtained by direct reaction of carbon monoxide with sulfur at the boiling point of the latter, by reaction of water vapor with carbon disulfide below 400 °C, by hydrolysis of ammonium or potassium thiocyanate with dilute sulfuric acid at 50–75 °C, or by decomposition of certain thiocarbonates and thiocarbamates with acid.

Chemical Properties

Carbonyl sulfide burns readily and forms an explosive mixture with oxygen. On oxidation with bromine water or acid permanganate, carbonyl sulfide gives carbon dioxide and sulfuric acid. Carbonyl sulfide is reduced by hydrogen giving carbon monoxide and hydrogen sulfide. Carbonyl sulfide and water react slowly giving carbon dioxide and hydrogen sulfide. Carbonyl sulfide undergoes thermal decomposition by either of 2 reactions:

$$2\,COS \rightarrow 2CO + 2S$$

$$2\,COS \rightarrow CO_2 + CS_2$$

Dissociation by the first reaction is rapid and reaches a maximum of 64% at 900 °C; dissociation by the second reaction is slow and reaches a maximum at 600 °C. Carbonyl sulfide is decomposed to an appreciable extent by alkalis to the alkali sulfide and carbonate. Carbonyl sulfide is used in the synthesis of thioacids and of S-trisubstituted carbinols by means of Grignard compounds (2).

For a review of the chemistry of carbonyl sulfide see Reference 3.

Thermodynamic and Detailed Physical Data

Molecular Structure

The COS molecule is linear, with bond distances of 1.16×10^{-10} m and 1.56×10^{-10} m for C=O and C=S, respectively. These interatomic distances are in agreement with the distances calculated from the following three resonance structure:

$$\ddot{O} :: C :: \ddot{S} \leftrightarrow : \overset{+}{O} ::: C : \ddot{S} : \overset{-}{} \leftrightarrow : \overset{-}{O} : C ::: \overset{+}{S} :$$

The COS molecule has $C_{\infty v}$ symmetry and has a symmetry number of one.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous carbonyl sulfide.

Matheson

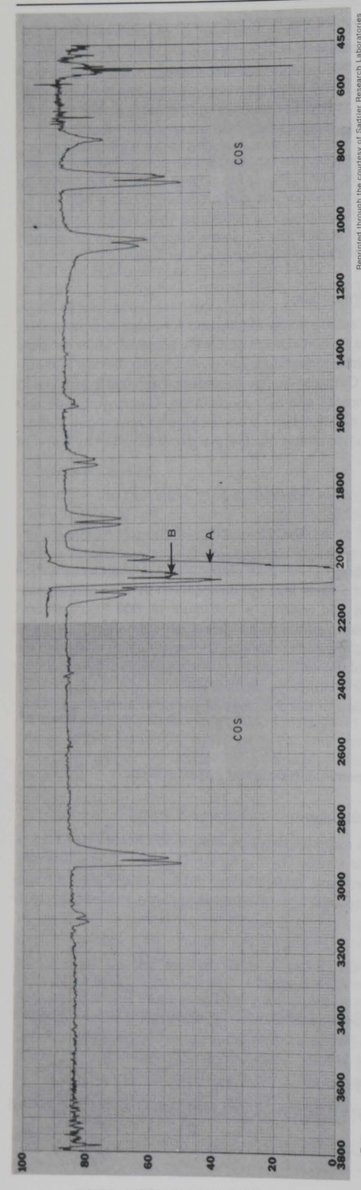


Fig. 2. Infrared spectrum of gaseous COS in the frequency range 3 800-450 cm^{-1}; 10 cm path length cell, with KBr windows; pressure: curve A: 4.0 kPa (30 mmHg), curve B (partial scan): 0.0667 kPa (0.5 mmHg) (7).

Vapor Pressure

The vapor pressure of liquid COS in the temperature of 111.0 °C to −49.0 °C is represented by the following equation (4):

$$\log_{10} p = 10.153\ 09 - \frac{1\ 318.260}{T} - 0.014\ 778\ 4T + 0.000\ 018\ 838T^2$$

in which p = cmHg and T = °K.

Some calculated vapor pressure values are listed below:

Temperature, °C	Vapor Pressure kPa	mbar	mmHg = torr
−111.0	1.769	17.7	13.27
−101.0	4.254	42.5	.91
−91.0	9.310	93.1	69.83
−281.0	18.572	185.7	139.30
−71.0	34.290	342.9	257.20
−61.0	59.302	593.0	444.80
−50.0	101.538	1 015.4	761.60

Vapor pressure from −40 to 60 °C are shown below (5).

Temperature, °C	Vapor Pressure kPa	bar
−40	151.99	1.52
−20	314.11	3.14
0	618.08	6.18
20	1 155.1	11.6
40	1 824	18.2
60	2 736	27.4

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv

Temperature, °C	ΔHv, kJ/kg
−70.0	321.58
−60.0	314.34
−50.2	308.07
−40.0	302.08
−30.0	293.38
−20.0	284.93

Thermodynamic Properties of Carbonyl Sulfide as Ideal Gas @ 25 °C (8)

Heat Capacity, C_p°	41.497 J/(mol·°K)
	0.691 kJ/(kg·°K)
Entropy, S°	231.471 J/(mol·°K)
	3.853 kJ/(kg·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/T$	−231.471 J/(mol·°K)
	−3.853 kJ/(kg·°K)
Enthalpy, H°	9.927 kJ/mol
	165.257 kJ/kg
Enthalpy of Formation, ΔH_f°	−138.407 kJ/mol
	−2 304.095 kJ/kg
Free Energy of Formation, ΔF_f°	−165.640 kJ/mol
	−2 757.450 kJ/kg

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of carbonyl sulfide, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases–First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 30–32, Matheson, Lyndhurst, New Jersey.

[3] R. J. Ferm, *Chem. Rev.* 57, 621–640 (1957).

[4] J. D. Kemp and W. F. Giauque, *J. Amer. Chem. Soc.* 59, 79 (1937).

[5] P. Macaluso in Kirk-Othmer's *Encyclopedia of Chemical Technology*, *1969*, Volume 19, p. 372, John Wiley & Sons, Inc., New York, New York.

[6] JANAF Thermochemical Tables, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[7] *The Sadtler Standard Spectra*, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

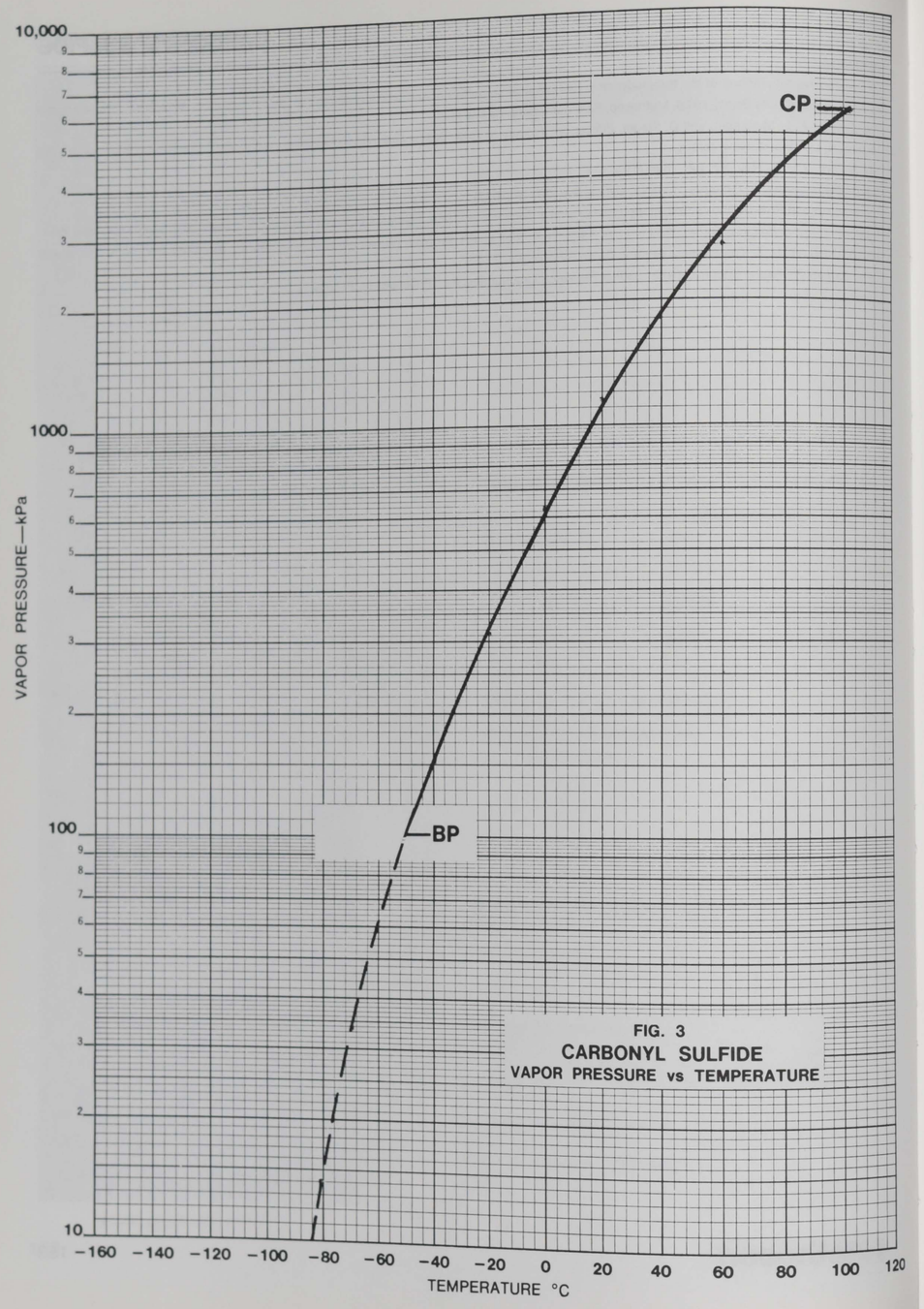


FIG. 3
CARBONYL SULFIDE
VAPOR PRESSURE vs TEMPERATURE

CHLORINE

(Formula: Cl_2)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.070 906 kg
One Mole of Cl_2	0.070 906 kg
Vapor Pressure @ 21.1 °C	689.0 kPa; 7.0 bar; 6.8 atm; 100.0 psia
Specific Volume @ 21.1 °C, 101.325 kPa	337.1 dm^3/kg; 5.4 ft^3/lb
Boiling Point @ 101.325 kPa	239.10 °K; −34.05 °C; −29.3 °F
Triple Point	172.17 °K; −100.98 °C; −149.8 °F
Absolute, Density, Gas @ 20°C, 101.325 kPa	2.980 0 kg/m^3; 2.980 0 g/l
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	2.473
Density, Liquid @ Saturation Pressure @ −40 °C	1.574 kg/l
Critical Temperature	417.15 °K; 144 °C; 291.2 °F
Critical Pressure	7 710 kPa; 77.1 bar; 1 118.4 psia; 76.1 atm
Critical Volume	1.745 dm^3/kg
Critical Density	0.573 kg/dm^3
Critical Compressibility Factor	0.276
Latent Heat of Fusion @ −100.98 °C	90.341 kJ/kg; 21.952 kcal/kg; 39.514 Btu/lb
Latent Heat of Vaporization @ −34.05 °C	287.84 kJ/kg; 68.8 kcal/kg; 123.8 Btu/lb
Molar Specific Heat, Gas @ 101.325 kPa, 25 °C	
@ Constant Pressure	35.317 J/(mol·°K); 0.498 kJ/(kg·°K); 8.441 cal/(mol·°C)
@ Constant Volume	27.004 J/(mol·°K); 0.381 kJ/(kg·°K); 6.454 cal/(mol·°C)
Specific Heat Ratio, Gas @ 101.325 kPa, @ 25 °C, Cp/Cv	1.308
Specific Heat, Liquid @ −30 °C	0.926 3 kJ/(kg·°K); 0.221 kcal/(kg·°C); 0.221 Btu/(lb·°F)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.013 27 mPa·s; 0.013 27 $mN·s/m^2$; 0.013 27 cP
Viscosity, Liquid @ 0 °C	0.385 mPa·s; 0.385 $mN·s/m^2$; 0.385 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 26.7 °C	0.008 8 W/(m·°K); 21×10^{-6} cal·cm/(s·cm^2·°C); 5.1×10^{-3} Btu·ft/(h·ft^2·°F)
Refractive Index, Gas @ 101.325 kPa @ 25 °C	1.000 713
Surface Tension @ 0 °C	21.90 mN/m; 21.90 dyn/cm
Solubility in Water @ Total Pressure of 101.325 kPa @ 0 °C	4.610 cm^3/1 cm^3 of water

Description

Liquid chlorine is a clear amber-colored liquid about 1.5 times as heavy as water. Gaseous chlorine is greenish-yellow, about 2.5 times as heavy as air. Chlorine has a disagreeable and suffocating odor with an irritating effect on the nose and throat. Chlorine is not flammable. It is shipped in steel cylinders under its own vapor pressure of 590 kPa (85 psig) at 21.1 °C.

Specifications

Matheson supplies three grades of chlorine.

1. Research Grade

This grade has a minimum purity of 99.96 mole % (liquid phase).

2. Ultra High Purity Grade

This grade of chloride has a minimum purity of 99.9 mole %.

3. High Purity Grade

This grade has a minimum purity of 99.5 mole % (liquid phase).

Uses

The uses of chlorine are numerous; some of the most important ones are the following:

1. Water purification
2. The sanitation of industrial wastes, sewage, and swimming pools
3. The bleaching of pulp and textiles
4. The manufacture of carbon tetrachloride, chlorobenzenes, ethylene oxide and glycol, synthetic glycerine, tetraethyl lead, vinyl chloride, trichloroethylene, perchloroethylene, and in the reaction with numerous other organic compounds
5. The manufacture of chloride of lime
6. The manufacture of phosgene

Toxicity (2)

A concentration of 1000 ppm by volume in air is rapidly fatal after a few deep breaths. Exposure to a concentration of 40–60 ppm by volume in air for 30–60 minutes is highly dangerous. The least amounts required to cause irritation of the throat and to cause coughing are 15 and 30 ppm, respectively. The maximum amount that can be inhaled for 1 hour without serious disturbances is 5 ppm.

Chlorine vapor is so irritating that concentrations of 3–5 ppm by volume in air are readily detectable. The 1979 ACGIH has established a Threshold Limit Value (TLV) of 1 ppm (3 mg/m^3) for chlorine.

The greenish-yellow color of chlorine becomes visible at high concentrations (2–3%).

The effects of different concentrations of gaseous chlorine are shown in Table 1.

Table 1. EFFECTS OF DIFFERENT CONCENTRATIONS OF CHLORINE IN MAN

Effect	Chlorine (ppm)
Minimum concentration causing slight symptoms after several hours	1
Minimum concentration detectable by odor	3.5
Maximum concentration that can be breathed for 1 hour without damage	4
Minimum concentration causing thorat irritation	15
Minimum concentration causing coughing	30
Concentration dangerous in 30 minutes	40–60
Concentration likely to be fatal after a few deep breaths	1 000

Skin contact with the vapor or liquid may result in ulceration and necrosis.

Chronic Toxicity

Low concentrations of chlorine gas in the air may have a minor irritating effect or may produce slight symptoms after several hours exposure, but careful examination of persons repeatedly exposed to such conditions reportedly have shown no chronic effect.

First Aid and Suggested Medical Treatment (2)

The following suggested treatments should be administered at once.

Inhalation

Remove patient from contaminated area to an uncontaminated one. If breathing has not ceased, the patient should be kept warm in a recumbent position (on his back, with head and back elevated) and observed for signs and symptoms of pulmonary edema. If breathing has ceased, artificial respiration should be started immediately, preferably by the mouth-to-mouth method. In either case, oxygen administration should be started as soon as possible. Stimulants will rarely be necessary where adequate oxygenation is maintained and any such drugs which may be required should be given only by the attending physician. Sodium bicarbonate may be given orally or intravenously to combat acidosis. Codeine is indicated for depression of cough reflex. Venesection is indicated (280–560 ml) when there is evidence of right heart embarrassment and nikethamide has been used as a medullary respiratory stimulant.

Contact with Skin or Mucous Membranes

If the patient has inhaled chlorine in addition to getting it on his skin or mucous membranes, first aid for inhalation should be given first.

If chlorine liquid or vapor has contaminated the skin or clothing, the person should get under a shower of water immediately and remove all contaminated clothing while under the shower. The affected areas of the skin should be washed with copious quantities of water, followed by large quantities of soap and water. Never attempt to neutralize the chlorine with chemicals. No salves or ointments should be applied for 24 hours.

Contact with Eyes

If gaseous or liquid chlorine contacts the eyes, they should be flushed immediately with copious quantities of running water for at least 15 minutes, while holding the eyelids wide apart during this time to insure contact of water with all accessible tissues of the eyes and lids. Call a physician, preferably an eye specialist, at once. If a physician is not immediately available, the eyes should be irrigated for a second 15-minute period. After the first irrigation period is complete, it is permissible to instill into the eye 2 or 3 drops of 0.5% tetracaine hydrochloride (Pontocaine) or some other equally effective aqueous topical anesthetic. No oils or oily ointment should be instilled unless perscribed by the physician.

Precautions in Handling and Storage

1. Since chlorine is an irritant to mucous membranes (particularly in the respiratory tract, in a lesser degree to the skin) and to the eyes, all personnel working with chlorine should be thoroughly acquainted with the proper methods of handling chlorine, the use of a gas mask and procedures to be followed in an emergency. Each person liable to exposure should be provided with a gas mask of a design approved for chlorine service by NIOSH. All gas masks should be inspected frequently and the instructions accompanying a mask, concerning its care and use, should be followed implicitly. It should be noted that gas masks of the cannister type do not supply oxygen but merely absorb the chlorine present in the air breathed. When the chlorine content of the air is greater than 1% a fresh air hose mask or oxygen supply mask is necessary. All personnel who may be required to use gas masks should be familar with their application and use. Gas masks should be located outside the probable area of contamination so that they may be reached in case of emergency and should be available in areas where chlorine is being stored or transported. An instant-acting safety shower and an eye-wash bath should be available.
2. If leaks develop in chlorine lines, they must be given prompt attention because they will become progressively worse. When a leak develops, the contaminated area should first be cleared of all personnel. Only specially trained and equipped personnel should be permitted in the area until the danger is cleared.
3. Work should be done in a well-ventilated area, preferably a hood with forced ventilation.
4. A chlorine cylinder should never be directly connected to a vessel containing a liquid since suckback may occur causing a violent reaction within the cylinder. To prevent suckback, a trap, check valve or vacuum break should be inserted into the line. The trap should be of adequate size to take the total liquid volume sucked back.
5. The rate of gas flow can be increased by improving air circulation about the container or by increasing the temperature of the room if it is below normal. Never apply heat directly to the cylinder for any reason. Do not manifold cylinders to increase output unless check valves have been inserted at the cylinder outlets to prevent exchange of material from one cylinder to another, causing a cylinder to become overfull. If the rate of discharge must be increased, liquid should be withdrawn by inverting the cylinder and then vaporizing the liquid.
6. Hoisting of cylinders is not recommended. If hoisting cannot be avoided, always use a lifting clamp, cradle, or carrier—never use a lifting magnet, rope, or chain sling.
7. Do not store chlorine cylinders near cylinders of hydrogen, acetylene, ammonia, fuel gases, ether, turpentine, hydrocarbons, organic matter, or finely divided metals.
8. Never mix chlorine and another gas in the cylinder.
9. Do not store chlorine cylinders near elevators or gangways or in locations where heavy objects may fall and strike them.
10. The amount of chlorine remaining in a cylinder should be determined by weight, since the cylinder pressure will remain constant as long as liquid remains in the cylinder.
11. Open cylinder valves slowly. The use of large wrenches or pipe wrenches will damage the valve. One complete turn of the valve stem in a counterclockwise direction opens the valve sufficiently to permit maximum discharge. Do not use a wrench longer than 6 inches on the cylinder valve.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Chlorine leaks may be located by means of an atomizer or squeeze bottle with aqueous ammonia. A white cloud will show the location of the leak. Every effort should then be made to repair the leak. Notify the supplier if leaks that are not reparable appear in the cylinder. Never put water on a chlorine leak since the mixture of water and chlorine may increase the rate of corrosion, and possibly make the leak larger.

Leaks around valve stems can be stopped by tightening the packing gland nut. The nut should be turned clockwise as viewed from above. If the leak cannot be stopped, the chlorine should be absorbed in a caustic soda or sodium carbonate solution.

A leaking container cannot be shipped; contact the supplier for instructions for returning it. In case of emergency, contact the supplier immediately.

Analytical Detection

The concentration of chlorine in air can be determined with Matheson-Kitagawa Toxic Gas Detector Model 8014K. Concentrations of 1–40 ppm of chlorine are measurable with the Model 109S detector tube. The chlorine concentration in air is read directly from the tube after sampling.

Chlorine can be determined by indirect titration with sodium thiosulfate. The sample is introduced into excess aqueous potassium iodide and the liberated iodine is then titrated with standard sodium thiosulfate solution.

Disposal of Leaking Cylinders

Leaks in cylinders containing chlorine which can not be corrected will require special handling. The procedure described in Appendix II-D can be used for disposal of chlorine.

Materials of Construction

Extra heavy black iron or steel pipe is recommended for dry liquid or gaseous chlorine, although copper and other materials that will withstand high pressure can be used. Steel, cast iron, wrought iron, most copper alloys, most nickel alloys, certain stainless steels and lead are common materials of construction. Pipe threads should be clean and sharp. Drop forged steel fittings should be used throughout the system and standard ammonia type flange unions are desirable.

Teflon tape is recommended as a thread sealant. Litharge and glycerine is a satisfactory pipe dope, but causes difficulty in making repairs where fittings have to be removed. Gaskets should be made of asbestos composition or lead containing 3% antimony. Rubber gaskets should never be used in liquid chlorine lines.

Drop forged steel globe or needle valves of a type specifically designed for liquid chlorine service are recommended. Valves with special brass or nickel alloys of sturdy design can also be used.

Liquid chlorine lines must be protected with an expansion chamber between all shut-off valves.

Moist chlorine is very corrosive to all of the common materials of construction. At low pressures, wet chlorine can be handled in chemical stoneware, glass or porcelain equipment, and by certain special alloys and plastic compositions. The noble metals platinum and silver are resistant, as is tantalum which is resistant to both wet and dry chlorine at temperatures below 150 °C. High silica iron, monel metal and Hastelloy C also have good resistance to moist chlorine.

Cylinder and Valve Description

Chlorine is shipped in steel cylinders, which comply with DOT specifications. They have a minimum sercive pressure of 3 420 kPa (496 psig). The chlorine cylinder valve outlet designated as the alternate standard by the Compressed Gas Association (CGA) is valve outlet No. 660. This outlet has a thread size of 1.030 inches diameter and is right-handed with external threads. The mating connection seats on a flat washer. Figure 1 illustrates the valve outlet and mating connection used in this service.

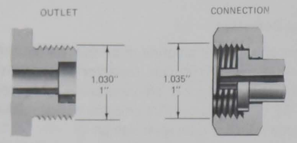


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

The lecture bottle containing one pound of chlorine is 2 inches in diameter and 15 inches long and is equipped with a Teflon-packed monel valve having a special outlet designated as $^{5}/_{16}$ inch-32 threads per inch female.

Safety Devices

Cylinders containing chlorine have, as a safety device, a fusible metal plug, melting at approximately 73.9 °C (165 °F). Cylinders over 55 inches long, exclusive of the neck, require this device in both ends.

Recommended Controls

Matheson supplies single stage regulators Model H15-660 (without cylinder pressure gauges) and Model H15C-660 (with cylinder pressure gauges) for use with the Research Purity Grade and Ultra High Purity Grade of chlorine. Each of these regulators has a nickel coated brass body, with internal parts constructed of monel. Kel-F and Teflon are used for critical sealing and seating surfaces, and a protective barrier for the metal diaphragm constructed of chemically deposited pure nickle or nickel-silver alloy. Both types of regulators are supplied with an aluminum-silicon bronze diaphragm packless outlet valve with a ¼" monel Gyrolok tube fitting. Both these regulators have delivery pressure ranges of 28–340 kPa (4–50 psig).

A check valve should be installed in the outlet to prevent suckback of foreign materials into the regulator.

Matheson supplies regulator Model B15-660 (without cylinder pressure gauge) or Model B15C-660 (with cylinder pressure gauge) for use with High Purity Grade chlorine. This regulator has a chemically coated nickel body, with internal parts of monel. The diaphragm, is Kel-F backed with silver plated nickel-silver alloy and the seat is of Kel-F. The needle valve on the outlet end is of monel. The delivery pressure range of the regulator is 28–340 kPa (4–50 psig).

To prevent suckback of foreign materials into the regulator, a Model 401E monel check valve is recommended.

Manual Controls

Monel needle valve Model 55A-660 can be supplied for all grades of chlorine where noncritical manual flow control of the liquid or gas is required. This valve is furnished with a ¼" tube fitting. Lecture bottles of the Ultra High Purity and High Purity grades utilize a monel needle valve Model 60L.

Flowmeters

Matheson Series 7600 laboratory monel flowmeter units with 150 mm tubes and floats are recommended for use where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ±1.2%.

Shipping Regulations

Chlorine is shipped under DOT regulations as a nonflammable compressed gas, taking a DOT "Chlorine Label".

Commercial Preparation

Chlorine is produced commercially by electrolysis of solutions of sodium chloride, potassium chloride, or magnesium chloride.

Chemical Properties

Some of the more important reactions of chlorine are listed below:

1. Reacts with practically all metals and many nonmetals to form the corresponding chlorides.
2. Reacts with excess phosphorus, forming phosphorus trichloride; also reacts with arsenic, antimony and silicon.
3. Phosphorus halides combine with excess chlorine.
4. Combines with hydrogen, forming hydrogen chloride.
5. Combines with water in two ways:

$$Cl_2 + H_2O \rightleftarrows 2H^+ + 2Cl^- + \tfrac{1}{2}\,O_2$$

and

$$Cl_2 + H_2O \rightleftarrows H^+ + Cl^- + HOCl$$

6. Chlorinates hydrocarbons.
7. Adds to olefins and acetylenes.
8. Reacts with hydrogen sulfide giving sulfur and hydrogen chloride.
9. Combines with carbon monoxide, forming phosgene.
10. Combines with sulfur dioxide, forming sulfuryl chloride.

Thermodynamic and Detailed Physical Data

Molecular Structure

The homopolar chlorine molecules has $D_{\infty h}$ symmetry and a symmetry number of two. The interatomic Cl-Cl bond distance is 1.986×10^{-10} m (1.986 Å).

Infrared Spectrum

The chlorine molecule is not infrared active but is Raman active.

It shows a fundamental vibrational frequency of 561.1 cm^{-1}.

Vapor Pressure

The vapor pressure of liquid chlorine from −93.6 °C to −17.4 °C is represented by the following Antoine vapor pressure equation (3):

$$\log_{10}p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10}p} - C$$

in which p = mmHg and t = °C, and the constants, A, B, and C have the values of 6.93180, 859.174, and 246.14, respectively.

Some calculated vapor pressure values are shown below.

Temperature,	Vapor Pressure		
°C	kPa	mbar	mmHg = torr
−93.6	2.67	26.7	20
−84.9	5.33	53.3	40
−75.3	10.67	106.7	80
−71.9	13.33	133.3	100
−60.6	26.66	266.6	200
−47.7	53.33	533.3	400
−39.3	79.99	799.9	600
−34.0	101.325	1 013.25	760
−32.9	106.66	1 066.6	800
−27.6	133.32	1 333.2	1 000
−17.4	199.98	1 999.8	1 500

Vapor pressures from −17.4 °C to 144.0 °C (critical temperature) may be calculated by the following equation (4);

$$\log_{10}p = 4.596\,15 - \frac{1\,056.66}{T} - 0.069\,5\,\log_{10}T$$

in which p = atm and T = °K.

Some calculated vapor pressure values are shown below.

Temperature,	Vapor Pressure		
°C	kPa	bar	atm
−10.0	262	2.62	2.586
0.0	367	3.67	3.619
10.0	501	5.01	4.946
20.0	670	6.7	6.613
30.0	859	8.59	8.478
60.0	1 799	17.99	17.752
100.0	3 904	39.04	38.531
120.0	5 420	54.20	53.490
144.0	7 707	77.07	76.060

For additional vapor pressure values see Table 2 and Figure 2.

Viscosity (5)

For viscosity of liquid and gaseous chlorine, see Figure 3.

Thermodynamic Properties of Chlorine as Ideal Gas @ 25 °C (6)

Heat Capacity, C°_p	33.936 J/(mol·°K)
	0.479 kJ/(kg·°K)
Entropy, S°	222.961 J/(mol·°K)
	3.144 kJ/(kg·°K)
Free Energy Function, $F^\circ_{298} - H^\circ_{298}/T$	−222.961 J/(mol·°K)
	−3.144 kJ/(kg·°K)
Enthalpy, H°	9 180 J/mol
	129.467 kJ/kg
Enthalpy of Formation, ΔH°_f	0.000 J/mol
Free Energy of Formation, ΔF°_f	0.000 J/mol

For the thermodynamic properties of saturated and superheated chlorine, see Tables 2 and 3.

REFERENCES

[1] For extensive tabulations of the thermdynamic and physical properties of chlorine, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, 1977, pp. 38–42, Matheson, Lyndhurst, New Jersey.

[3] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds, 1968*, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[4] *Chlorine Handbook, 1950*, p. 33, Diamond Alkali Company, Cleveland, Ohio.

[5] *Ibid.*, p. 41.

[6] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS – NBS 37, U. S. Government Printing Office, Washington, D.C.

[7] See reference 4, p. 34.

Table 2. THERMODYNAMIC PROPERTIES OF SATURATED CHLORINE (7)

Temperature		Pressure		Entropy kJ/(kg °K)		Enthalpy kJ/kg		Latent Heat of Vaporization kJ/kg	Specific Volume		Density	
°C	°F	kPa	bar	Liquid	Vapor	Liquid	Vapor		l/kg Liquid	dm^3/kg Vapor	kg/l	kg/m^3
−40.0	−40	77.8	0.778	1.819	3.060	233.91	524.65	290.74	0.636	344.98	1.574	2.899
−28.9	−20	126	1.26	1.860	3.027	244.83	529.81	284.98	0.647	220.72	1.546	4.531
−17.8	0	202	2.02	1.903	2.995	255.76	534.60	278.84	0.659	152.84	1.517	6.826
−6.7	20	295	2.95	1.944	2.966	266.68	538.99	272.31	0.672	100.88	1.487	9.913
4.4	40	422	4.22	1.982	2.938	277.61	543.06	265.45	0.687	72.32	1.456	13.827
15.6	60	589	5.89	2.017	2.911	288.53	546.68	258.15	0.702	52.87	1.424	18.913
26.7	80	804	8.04	2.050	2.885	299.46	549.98	250.52	0.719	39.43	1.390	25.360
37.8	100	1 083	10.83	2.082	2.859	310.24	552.08	241.84	0.737	29.57	1.356	33.813
48.9	120	1 399	13.99	2.114	2.835	321.03	553.05	232.02	0.758	23.10	1.320	43.288
60.0	140	1 796	17.96	2.146	2.811	331.81	553.52	221.71	0.781	18.00	1.280	55.569
71.1	160	2 269	22.69	2.179	2.788	342.97	552.70	209.73	0.807	14.16	1.239	70.624
82.2	180	2 824	28.24	2.218	2.772	355.24	552.29	197.05	0.838	11.24	1.194	88.988
93.3	200	3 467	34.67	2.267	2.763	369.31	551.33	182.02	0.875	8.98	1.143	111.40
104.4	220	4 207	42.07	2.322	2.758	385.88	550.68	164.80	0.920	7.19	1.088	139.17
115.6	240	5 048	50.48	2.382	2.753	406.08	550.43	144.35	0.976	5.59	1.025	178.98
126.7	260	5 995	59.95			432.32	550.19	117.87	1.054	4.32	0.949	231.48
264.4	280	7 055	70.55			468.33	547.73	79.40	1.228	3.12	0.814	321.02
144.0	291	7 956	79.56			507.52	507.52	0.00	1.744	1.744	0.573	573.30

Table 3. THERMODYNAMIC PROPERTIES OF SUPERHEATED CHLORINE VAPOR (5)
H, ENTHALPY, KJ/KG; **S**, ENTROPY KJ/(KG °K); SPECIFIC VOLUME, DM^3/KG

Pressure, kPa		Temperature, °C						
		−17.8	10.0	37.8	65.6	93.3	148.9	204.4
68.9	H	536.48	550.66	564.84	579.25	593.43	621.79	650.14
	S	3.120	3.169	3.213	3.253	3.288	3.358	3.416
	V	429.0	477.0	525.0	573.0	621.0	716.4	811.0
101.325	H	536.02	550.20	564.61	578.79	592.96	621.56	650.14
	S	3.073	3.122	3.166	3.206	3.243	3.310	3.368
	V	290.0	323.4	356.4	389.4	422.3	487.1	552.4
172	H	535.09	549.26	563.44	577.86	592.27	621.09	649.91
	S	3.008	3.058	3.102	3.142	3.179	3.248	3.306
	V	168.4	187.9	207.6	227.2	247.1	185.9	324.1
276	H		547.87	562.28	576.69	591.34	620.39	649.68
	S		3.001	3.045	3.085	3.121	3.193	3.251
	V		115.6	128.3	141.0	153.6	178.2	202.3
413	H		545.55	560.42	575.30	589.94	619.70	649.45
	S		2.950	2.994	3.034	3.070	3.141	3.204
	V		75.48	84.21	92.95	101.6	118.3	134.6
551	H			558.56	573.67	588.78	618.76	648.98
	S			2.954	2.996	3.031	3.105	3.170
	V			62.15	68.92	75.59	88.40	100.8
827	H			555.54	570.88	586.46	617.14	647.82
	S			2.900	2.940	2.978	3.055	3.123
	V			40.05	44.81	49.53	58.41	66.79
103	H				568.09	584.13	615.51	646.66
	S				2.898	2.938	3.018	3.087
	V				32.70	36.41	43.38	49.77
1 379	H				564.37	581.81	614.12	645.26
	S				2.863	2.905	2.988	3.062
	V				28.76	31.01	34.31	39.50
1 655	H				560.19	579.02	612.26	643.87
	S				2.833	2.876	2.958	3.040
	V				20.45	23.21	28.23	32.62
1 930	H				555.31	575.53	610.16	642.24
	S				2.807	2.851	2.936	3.021
	V				16.87	19.41	23.86	27.67
2 414	H					569.26	606.45	639.45
	S					2.813	2.904	2.993
	V					14.75	18.57	21.86
2 758	H					564.37	603.66	637.36
	S					2.791	2.888	2.976
	V					12.40	15.92	18.87

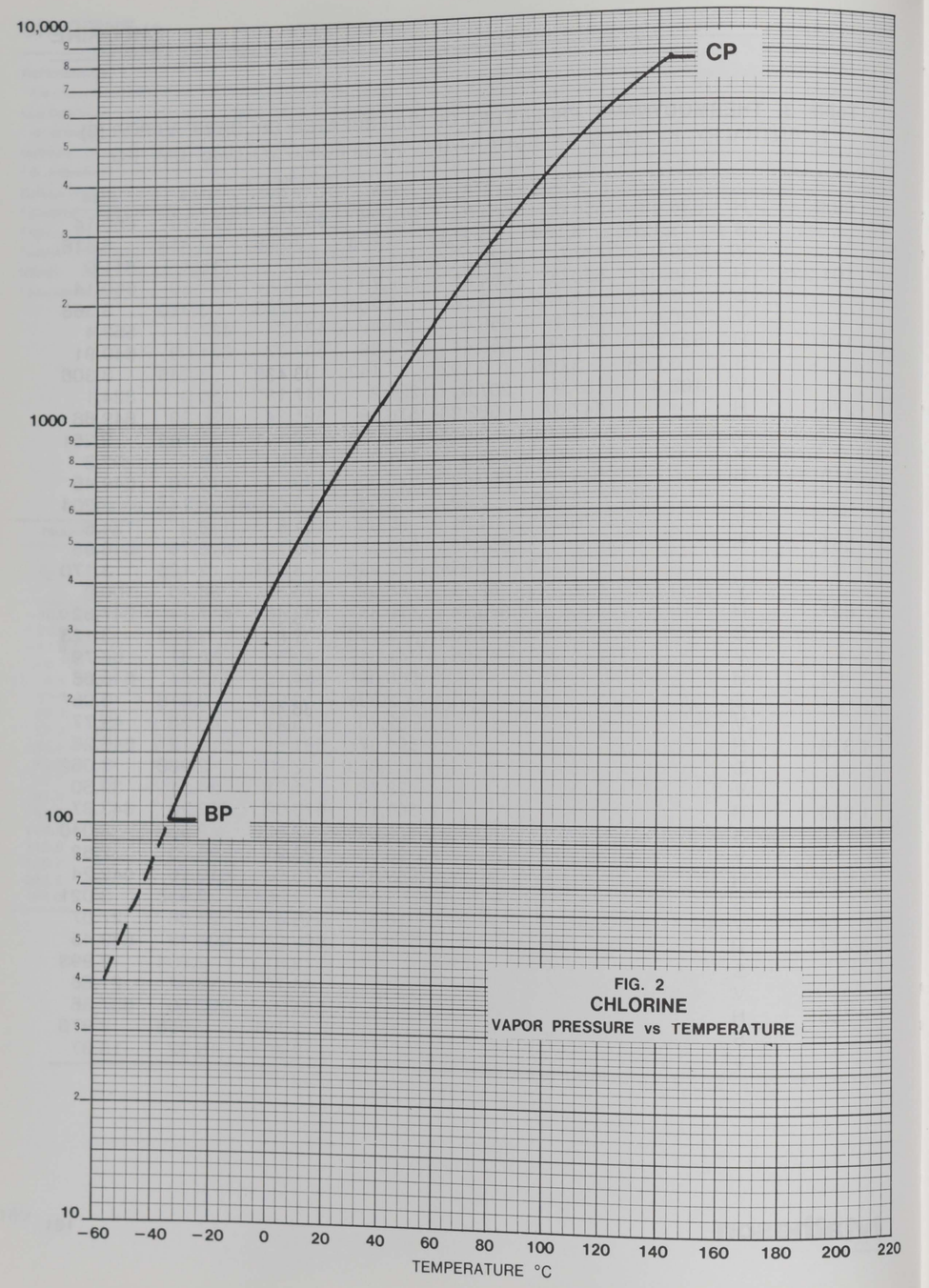


FIG. 2
CHLORINE
VAPOR PRESSURE vs TEMPERATURE

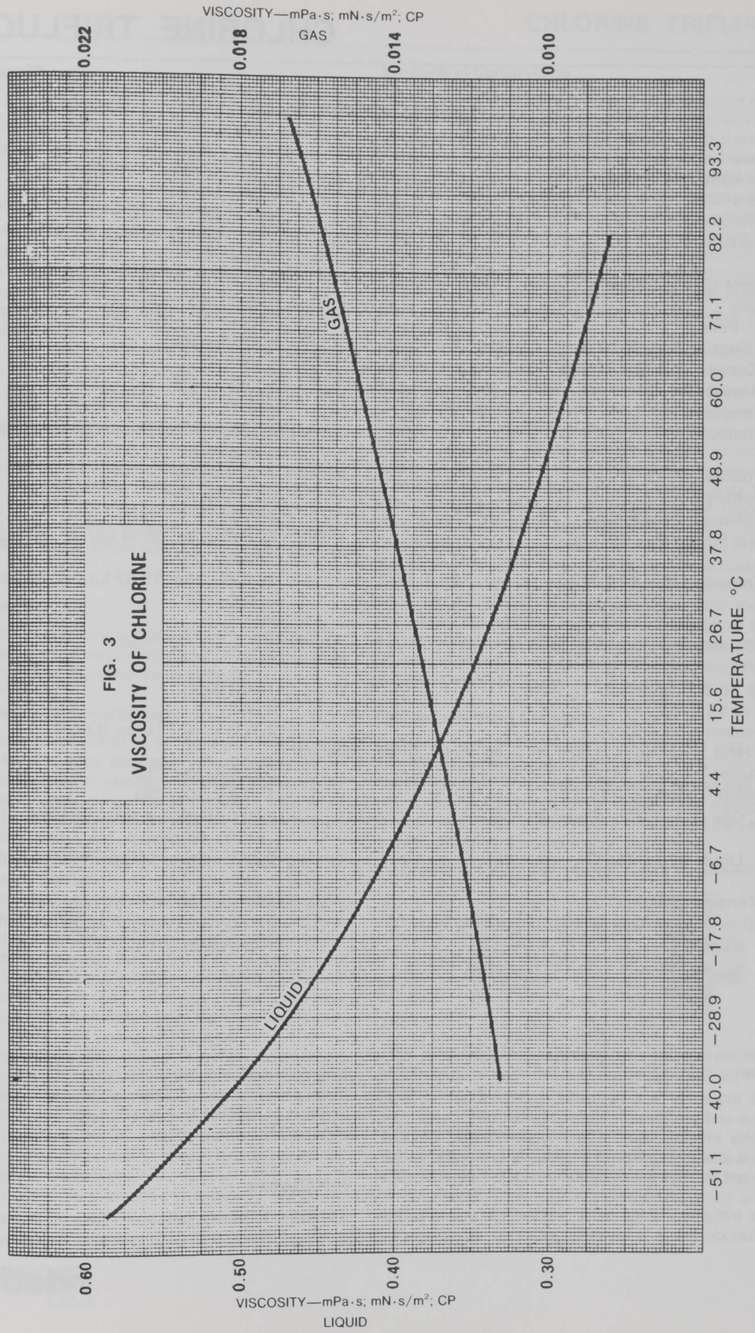


FIG. 3
VISCOSITY OF CHLORINE

CHLORINE TRIFLUORIDE

(Formula: ClF_3)

PHYSICAL PROPERTIES (1)

Molar Mass	0.092 448 kg
Molecular Weight	0.092 448 kg
One Mole of ClF_3	262.2 dm^3/kg; 4.2 ft^3/lb
Specific Volume, Gas @ 21.1 °C, 101.325 kPa	148.2 kPa; 1.48 bar; 21.5 psia; 1.46 atm
Vapor Pressure @ 21.1 °C	284.90 °K; 11.75 °C; 53.2 °F
Boiling Point @ 101.325 kPa	196.83 °K; −76.3 °C; −105.4 °F
Triple Point	190.47 °K; −82.7 °C; −116.8 °F
Transition Point	3.863 kg/m^3
Absolute Density, Gas @ 20.0 °C, 101.325 kPa	3.21
Relative Density, Gas @ 101.325 kPa @ 20.0 °C (Air = 1)	1.885 3 kg/l
Density, Liquid @ 0 °C	447.15 °K; 174.0 °C; 345.2 °F
Critical Temperature	5 776 kPa; 57.76 bar; 57.0 atm; 837.7 psia
Critical Pressure	1.91 dm^3/kg
Critical Volume	0.524 kg/dm^3
Critical Density	0.274
Critical Compressibility Factor	82 340 J/kg; 82.34 kJ/kg; 1819.3 cal/mol
Latent Heat Fusion @ −76.3 °C	16 320 J/kg; 16.32 kJ/kg; 360.5 cal/mol
Heat of Transition @ −82.7 °C	23.1
Trouton's Constant	$3.9 \times 10^{-9}\ \Omega^{-1}$/cm
Specific Conductivity, Liquid @ 25.0 °C	
Dielectric Constant	
Gas @ 46.2 °C	1.002 825
Liquid @ 25.0 °C	4.304
Dipole Moment, Gas	2.168×10^{-30} C·m; 0.65 D
Specific Heat, Gas @ 101.325 kPa @ 25.0 °C @ Constant Pressure	0.726 kJ/(kg·°K)
Specific Heat, Liquid @ −46.2 °C	1.224 kJ/(kg·°K)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.011 66 mPa·s; 0.011 66 mN·s/m^2; 0.011 66 cP
Viscosity, Liquid @ 11.75 °C	0.478 mPa·s; 0.478 mN·s/m^2; 0.478 cP
Surface Tension @ 0.0 °C	26.7 mN/m; 26.7 dyn/cm
Thermal Conductivity, Gas @ 101.325 kPa @ 20.0 °C	9.77×10^{-3} W/(m·°K); 24×10^{-6} cal·cm/(s·cm^2·°C)

Description

Chlorine trifluoride is a corrosive, colorless gas at room temperature and pressure. It has somewhat of a sweet odor and is highly irritating even at low concentrations. Chlorine trifluoride is easily liquefied to a yellow-green liquid at low pressures and atmospheric temperatures. It freezes to a white solid.

Chlorine trifluoride is the most reactive compound of the halogen fluorides. It is a powerful oxidizing agent causing immediate ignition of many organic compounds, ignites many metals at elevated temperatures, and reacts violently with water or ice. It is shipped as a liquefied gas under its own vapor pressure of 48 kPa (7 psig).

Specifications

Chlorine trifluoride has a minimum purity of 98.0% and contains a maximum of 2.0% hydrogen fluoride as an impurity.

Uses

Chlorine trifluoride is of interest as a propellant for rockets and missiles. It has the ability to start reaction immediately on contact with fuels (hypergolicity). It has also been used in an oil well tubing cutter. It has been used for cutting pipe in oil wells as far as two miles below the surface.

Effects in Man and Toxicity (2)

Chlorine trifluoride is a pulmonary irritant and can cause pulmonary edema. It can cause severe chemical and thermal burns. Exposure to high concentrations is usually fatal, respiratory damage and pulmonary edema being the cause of death. Prolonged exposure to as little as 5–10 ppm causes irritation of the eyes and nasal and buccal mucosa. Contact of the skin with chlorine trifluoride causes severe burns in 0.2 second, and an exposure for as long as 0.6 second can result in thermal burns comparable with those produced by the oxyacetylene flame.

The lowest toxic concentration of chlorine trifluoride in humans by inhalation is reported to be 25 ppm/5 minutes.

The 1979 American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a Threshold Limit Value of 0.1 ppm (0.4 mg/m^3) for chlorine trifluoride (i.e., concentration in air to which nearly all workers may be repeatedly exposed during a normal 8-hour working day without adverse affects.)

First Aid Treatment (2)

The first aid treatment to be followed is that described for hydrofluoric acid and fluorine-containing compounds which form hydrofluoric acid on hydrolysis by moisture.

Precautions in Handling and Storage

1. Since chlorine trifluoride is so extremely corrosive to human tissue and the eyes, personnel, when handling equipment which contains or has recently contained chlorine trifluoride, should wear rubber gloves, safety glasses, a face shield and a protective apron which will serve for normal use and will protect for limited contact with splashes.
2. Work should be done in a well-ventilated area, preferably a hood with forced ventilation.
3. In removing the contents from a cylinder, attach a suitable needle valve to the valve outlet so that uniform rates of flow can be controlled. Dry nitrogen may be used to pressurize the cylinder in order to transfer the liquid, since suckback may occur causing a violent reaction within the cylinder. To prevent suckback, a trap, check valve or vacuum break should be inserted in the line. The trap should be of sufficient size to take the total liquid volume that can be sucked back.
4. An instant-acting safety shower should be available, as well as filled buckets of sodium bicarbonate to absorb spillage as well as combat any secondary fires.
5. An air-line respiratory or oxygen mask should be kept close by the operation site, in an area that is not likely to become contaminated, to be used in case of emergency where dangerous concentrations may exist.

In addition, the general rules listed in Appendix I should be observed.

Materials of Construction

Chlorine trifluoride can be used with a variety of metals due to the formation of a passive metal fluoride film which protects the metal from further corrosion. Monel and nickel are preferred materials of construction However, metals such as copper, brass and steel may be used. Highly fluorinated polymers such as Kel-F and Teflon are resistant to the liquid and vapor at ordinary temperatures under normally static conditions only. Their use in flow conditions is not recommended. Materials suitable for gaskets are soft copper, 2S aluminum, lead and Teflon either plain or impregnated with a high percentage of calcium fluoride. Braided copper backed with Teflon can be used for valve packings. A pipe thread sealant, if needed, should be Teflon tape.

It is of utmost importance that all equipment used in chlorine trifluoride service be thoroughly cleaned to remove grease, scale, pipe dope or other contaminants. All equipment should be disassembled, degreased and reassembled with proper packing before use. Degreasing and cleaning should be done with a nonaqueous solvent such as acetone, trichlorethylene or carbon tetrachloride. After cleaning, the system should be thoroughly purged with a stream of nitrogen. Since the corrosion resistance of the materials of construction recommended depend on the formation of a passive fluoride film, a passivating procedure should be used after the cleaning and drying of the system as mentioned above. This procedure consists of evacuating the dry nitrogen from the system and slowly bleeding a small amount of chlorine trifluoride vapor into the system. Because of the very low vapor pressure of chlorine trifluoride, it is recommended that the vapor be left in the system for about an hour to ensure that a passive film has been built up. The system can then be vented and is ready for use.

Cylinder and Valve Description

Chlorine trifluoride cylinders are equipped with the Compressed Gas Association (CGA) connection No. 670, the approved standard. The valve outlet has a thread size of 1.030 inches, left-handed with external threads. The mating connection seats on a flat washer. Figure 1 illustrates the valve outlet and the mating connection used in the service.

CONNECTION 670 1.030"-14 LH EXT. using Flat Seat with Washer

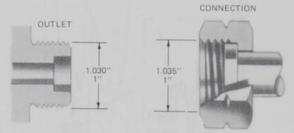


Figure 1

The lecture bottle is equipped with a Teflon-packed monel valve having a special outlet designated as 5/16"-32 threads to the inch, female.

Safety Devices

Since chlorine trifluoride cylinders are not equipped with safety devices, care must be taken to see that the cylinders are not heated. Direct application of heat must always be avoided.

Recommended Controls

Manual Controls

Matheson provides a manual needle valve, Model 55A-670, for direct connection to the valve outlet of the cylinder of chlorine trifluoride. This needle valve is provided with compression fitting or ¼" male or female NPT. A Model 60L needle valve is recommended for use with lecture bottles.

Shipping Regulations

Chlorine trifluoride is shipped in steel cylinders as a corrosive liquid, taking a "White Label", complying with the DOT regulations.

Chemical Preparation

Chlorine trifluoride is obtained by passing a mixture of slightly more than 3 moles of fluorine per 1 mole of chlorine through a nickel or monel tube at 290 °C, or by the reaction of ClF with F_2.

Chemical Properties

Chlorine trifluoride can raise metals to their highest valence states. Chlorine trifluoride is a powerful oxidizing and fluorinating agent. It reacts with almost all elements except the the inert gases, nitrogen, and a few metals. Nickel is unattacked up to 400 °C. Bromine and iodine react with chlorine trifluoride to give bromine trifluoride and iodine pentafluoride, respectively. Chlorine trifluoride converts oxides to fluorides and oxyfluorides, forms metal fluorides from other halides salts, and oxidizes such materials as ammonia, hydrazine, carbon monoxide, sulfur dioxide and ammonium salts. It reacts violently with water or ice. Chlorine trifluoride reacts with organic compounds giving a complex mixture of organic degradation products.

Thermodynamic and Detailed Physical Data

Molecular Structure

The ClF_3 molecule has a planar distorted T structure, with C_{2v} symmetry and a symmetry number of two. The Cl-F bond distance of the two long-bonded (axial) F atoms (denoted F^1 and F^3) is 1.698×10^{-10} m (1.698 Å), while that of the short-bonded (equatorial) F atom (denoted F^2) is 1.598×10^{-10} m (1.598 Å). The F^1-Cl-F^2 and F^2-Cl-F^3 bond angles are 87.48°, while the F^3-Cl-F^1 bond angle is 185.03° (3) (4).

Infrared Spectrum

The infrared spectrum of gaseous chlorine trifluoride is shown in Figure 2.

Vapor Pressure (5)

The vapor pressure of liquid ClF_3 between −60.0 and 30.0 °C is represented by the following Antoine vapor pressure equation:

$$\log_{10}p = A - \frac{B}{C + t} \quad \text{or} \quad t = \frac{B}{A - \log_{10}p} - C$$

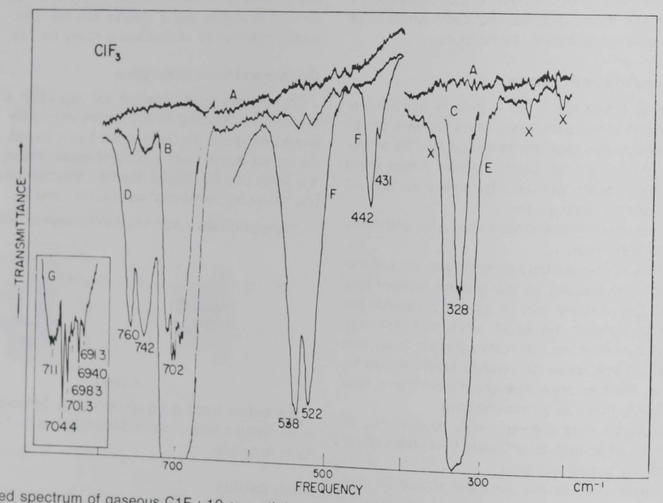


Fig. 2. Infrared spectrum of gaseous ClF_3; 10 cm path length nickel cell, with AgCl or polyethylene windows; A, background; curve B obtained at 0.267 kPa (2 mmHg) pressure, curve C at 1.333 kPa (10 mmHg), curve D at 2.266 kPa (17 mmHg), curve E at 19.332 kPa (145 mmHg), curve F at 60.00 kPa (450 mmHg), curve G (inset) obtained at 0.267 kPa (2 mmHg) shows detail of the 702 cm^{-1} band; X indicates HF impurity (6).

in which p = mmHg and t = °C and the constants A, B, and C have the values of 7.367 11, 1 096.917, and 232.75, respectively.

Some calculated vapor pressure values are shown below.

Temperature, °C	Vapor Pressure kPa	mbar	mmHg = torr
−60.0	1.39	13.9	10.4
−40.0	6.33	63.3	47.5
−20.0	21.69	216.9	162.7
0.0	60.14	601.4	451.1
11.55	101.325	1 013.25	760.0
20.0	141.9	1 418.9	1 064.2
30.0	207.6	2 076.2	1 557.3

For additional vapor pressure values, see Figure 3.

Latent Heat of Vaporization, ΔHv

Temperature, °C	ΔHv, kJ/kg
0.0	309.70
11.55	297.80
20.0	291.83

Thermodynamic Properties of Chlorine Trifluoride as Ideal Gas @ 25 °C (3)

Heat Capacity, C°_p	63.848 J/(mol·°K) 0.691 (kJ/(kg·°K)
Entropy, S°	281.495 J/(mol·°K) 3.045 kJ/(kg·°K)
Free Energy function, $(F^\circ_{298} - H^\circ_{298})/T$	−281.495 J/(mol·°K) −3.045 kJ/(kg·°K)
Enthalpy, H°	13.648 kJ/mol 147.630 kJ/kg
Enthalpy of Formation, ΔH°_f	−158.866 kJ/mol −1 718.5 kJ/kg
Free Energy of Formation, ΔF°_f	−118.901 kJ/mol −1 286.1 kJ/kg

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of chlorine trifluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, 1977, pp. 47–51, Matheson, Lyndhurst, New Jersey.

[3] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data. Ser., Natl. Bur. Stand. NSRDS – NBS 37, U. S. Government Printing Office, Washington, D.C.

[4] *Advances in Fluorine Chemistry*, M. Stacey, J. C. Tatlow, and A. G. Sharpe, editors, *1965*, Volume 4, p. 240, Butterworth Inc., Washington, D.C.

[5] J. W. Grisard, H. A. Bernhardt, and G. D. Oliver, *J. Amer. Chem. Soc. 73*, 5725–5727 (1951).

[6] H. Selig, H. H. Claassen, and J. H. Holloway, *J. Chem. Phys. 52*, 3517–3521 (1970).

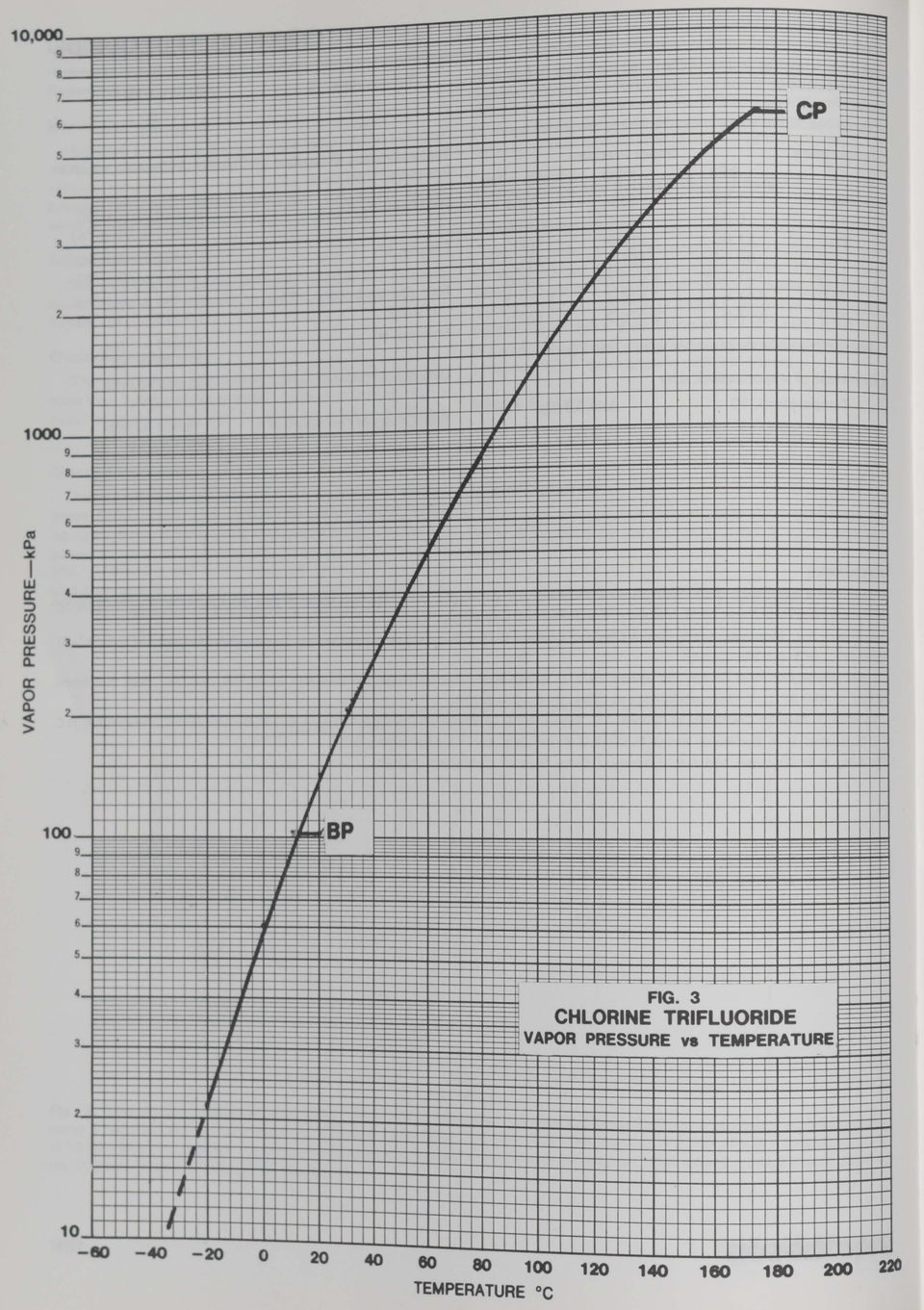


FIG. 3
CHLORINE TRIFLUORIDE
VAPOR PRESSURE vs TEMPERATURE

CHLORODIFLUOROMETHANE

(Synonym: Freon-22®)
(Formula: $CHClF_2$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.086 47 kg
One Mole of $CHClF_2$	0.086 47 kg
Specific Volume, Gas @ 21.1 °C, 101.325 kPa	274.7 dm^3/kg; 4.4 ft^3/lb
Vapor Pressure @ 21.1 °C	949 kPa; 9.49 bar; 137.7 psia; 9.37 atm
Boiling Point @ 101.325 kPa	232.49 °K; −40.7 °C; −41.19 °F
Transition Point	59.15 °K; −214.0 °C; −353.2 °F
Melting Point	115.72 °K; −157.4 °C; −251.4 °F
Absolute Density, Gas @ 101.325 kPa @ 20.0 °C	3.74 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20.0 °C (Air = 1)	3.11
Density, Liquid @ Saturation Pressure @ −40.7 °C	1.413 kg/l
Critical Temperature	369.15 °K; 96.0 °C; 204.8 °F
Critical Pressure	4 977 kPa; 49.77 bar; 49.12 atm; 721.9 psia
Critical Volume	1.905 dm^3/kg
Critical Density	0.525 kg/dm^3
Critical Compressibility Factor	0.267
Latent Heat of Fusion @ −157.4 °C	47 700 J/kg; 47.70 kJ/kg; 11.40 kcal/kg
Latent Heat of Vaporization @ −40.7 °C	233 840 J/kg; 233.84 kJ/kg; 55.89 kcal/kg
Refractive Index @ 21.1 °C, n_D	
Liquid	1.259
Vapor (101.325 kPa)	1.000 73
Relative Dielectric Strength (Nitrogen 1)	1.3
Dielectric Constant	
Liquid @ 23.9 °C	6.11
Vapor @ 25.6 °C (51 kPa)	1.003 5
Dipole Moment	4.9×10^{-30} C·m; 1.48 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25.0 °C	
@ Constant Pressure	57.524 kJ/(kmol·°K); 57.524 J/(mol·°K); 0.159 cal/(mol·°C)
@ Constant Volume	49.130 kJ/(kmol·°K); 49.130 J/(mol·°K); 0.136 cal·(mol·°C)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25.0 °C, Cp/Cv	1.171
Molar Specific Heat, Liquid @ −40 °C	94.788 kJ/(kmol·°K); 94.788 J/(mol·°K): 22.655 cal/(mol·°C)
Viscosity, Gas @ 101.325 kPa @ 0.0 °C	0.012 1 mPa·s; 0.0122 $mN \cdot s/m^2$; 0.0122 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25.0 °C	0.011 7 W/(m·°K): 28×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −40 °C	18.5 mN/m; 18.5 dyn/cm
Solubility in Water @ 101.325 kPa @ 25.0 °C	0.30% (by weight)
Solubility of Water in $CHClF_2$ @ 4.4 °C	0.069% (by weight)

Description

Chlorodifluoromethane is a colorless, nonflammable, nontoxic gas. In concentrations up to 20% by volume chlorodifluoromethane is odorless; in higher concentrations, its odor is mild and somewhat ethereal. It is shipped in steel cylinders as a liquefied gas under its own vapor pressure of 850 kPa (123 psig) at 21.1 °C.

Specifications

Chlorodifluoromethane has a minimum purity of 99.9 mole %.

Uses

Chlorodifluoromethane is used as a low-temperature refrigerant down to −101 °C, in industrial and commercial systems employing reciprocating type compressors. It is used as an intermediate in the production of Teflon. It is also used in aerosol prepellant formulations.

Effects In Man (2)

Inhalation of high concentrations of chlorodifluoromethane can cause such symptoms as dizziness, disorientation, incoordination, narcosis, nausea or vomiting. There appear to be no irreversible effects once the oxygen deficiency has been corrected. Skin contact with liquid chlorodifluoromethane can cause skin irritation or frostbite.

Toxicity (2)

Chlorodifluoromethane is relatively nontoxic according to the rating system devised by the Underwriters' Laboratories, Chicago, Illinois. It falls into Group 5A or 6 in this system. Group 5A includes those gases or vapors which are much less toxic than those in Group 4 but more toxic than those in Group 6. Group 4 includes those gases or vapors which in concentrations of about 2–2.5% for durations of exposure of about 2 hours are lethal or produce serious injury. Group 6 contains those gases or vapors which in concentrations up to at least 20% by volume in air for durations of exposure for about 2 hours do not appear to produce injury. The relatively nontoxic carbon dioxide is classified as a Group 5A gas by Underwriters' Laboratoreis. The 1979 ACGIH has established a Threshold Limit Value of 1000 ppm (3500 mg/m^3) for chlorodifluoromethane.

First Aid Treatment (2)

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration (if needed) and oxygen simultaneously. Treat symptomatically thereafter.

Skin Contact

In case of skin contact with liquid chlorodifluoromethane frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed in the handling and storage of chlorodifluoromethane.

Leak Detection

Leaks of chlorodifluoromethane may be detected by applying soap water solution to suspected points; leaks will be indicated by bubble formation. Leaks of chlorodifluoromethane in dark, confined or inaccessible spaces or locations may be located by means of a halide torch or lamp. The Matheson Leak Detectors Model 8016 and 8017 are useful for more sensitive leak detection.

Disposal of Leaking Cylinders

Cylinders of chlorodifluoromethane which develop leaks that cannot be readily corrected should be treated as described in Appendix II-C.

Materials of Construction

Most of the commonly used metals (steel, cast iron, brass, copper, tin, lead, aluminum) may be used satisfactorily with chlorodifluoromethane under normal conditions of use. At high temperatures some of the metals may act a catalysts for the breakdown of the compound. The tendency of metals to promote thermal decomposition of chlorodifluoromethane is in the following approximate order: silver > brass > bronze > aluminum > 1340 steel > copper > nickel > 18-8 stainless steel > inconel (least decomposition). Magnesium alloys and aluminum containing more than 2% magnesium are not recommended for use in systems containing chlorodifluoromethane where water may be present.

In general, gasket materials should not contain natural rubber. Neoprene or Isoprene rubber, pressed fibers (including asbestos) with a number of insoluble binders, and metallic gaskets may be used.

Cylinder and Valve Description

Chlorodifluoromethane is shipped in DOT approved, low pressure, steel cylinders, having a rated service pressure of 1 655 kPa (240 psig) or more. Cylinders containing chlorodifluoromethane are equipped with brass valves with Compressed Gas Association (CGA) outlet connection No. 660, the approved alternate connection. The valve outlet has a thread size of 1.030 inches with right-hand external threads, used with a flat seat and washer (see Figure 1). Lecture bottles have

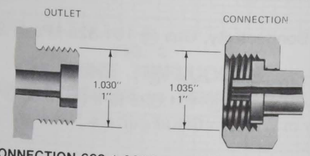


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

a special 5/16 inch-32 threads per inch female outlet and a 9/16 inch-18 threads per inch male dual valve outlet.

Safety Devices

Cylinders containing chlorodifluoromethane have fusible metal plugs, melting at about 74 °C as safety devices. Cylinders over 30 inches long (exclusive of the neck) require this device in both ends of the cylinder.

Recommended Controls

Automatic Pressure Regulators

Automatic regulator Model 1P-660 or Model 1L-660 is recommended for use with chlorodifluoromethane. These regulators are manufactured with brass bodies. Their delivery pressure ranges are 28–240 kPa (4–35 psig) and 28–550 kPa (4–80 psig), respectively. No cylinder pressure gauge is necessary since it will not indicate cylinder content but only vapor pressure which will remain constant as long as any liquid remains in the cylinder. Cylinder content is determined by weight. To prevent suckback of foreign materials, a check valve is recommended for use with the regulator.

Matheson regulator Model 70-660 will provide accurate low pressure regulation in the delivery pressure range of 3.4–34.5 kPa (0.5–5.0 psig). Regulator Model 3321, with a delivery pressure range of 28–410 kPa (4–60 psig), is recommended for use with lecture bottles.

Manual Controls

Matheson needle valve Model 50-660, a brass bar stock valve, is available for direct connection to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, ¼" compression fittings, or ¼" NPT male or female pipe. The valve is used to provide intermittent flow of gas or to control the flow of gas directly from the cylinder, but this requires close supervision. It should not be used as a pressure control, since dangerous pressures can develop if a line or the system itself becomes clogged. A Model 31B manual needle valve is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Chlorodifluoromethane is classified by the DOT as a nonflammable compressed gas and is shipped with the required "Green Label".

Chemical Preparation

Chlorodifluoromethane is prepared by treating chloroform with anhydrous hydrogen fluoride in the presence of a small amount of antimony chloride at elevated temperatures and pressures.

Chemical Properties

Chlorodifluoromethane is comparatively thermally stable. The rate of hydrolysis of chlorodifluoromethane in water is less than 0.000 01 kg/l water/year; in the presence of steel, the rate is about 0.000 1 kg/l water/year; under alkaline conditions, chlorodifluoromethane tends to be hydrolyzed more rapidly. Pyrolysis of chlorodifluoromethane results in the formation of polytetrafluoroethylene (Teflon).

Thermodynamic and Detailed Physical Data

Molecular Structure

The $CHClF_2$ molecule belongs to point group C_s and has a symmetry number of one. The C—H bond distance is 1.09×10^{-10} m (1.09 Å) and the C—Cl and C—F bond distances are 1.74×10^{-10} m (1.74 Å) and 1.35×10^{-10} m (1.35 Å), respectively. The H—C—Cl, Cl—C—F, and F—C—F bond angles are 107°, 110.5° and 107°, respectively (3).

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous chlorodifluoromethane.

Vapor Pressure

The vapor pressure of liquid chlorodifluoromethane between −87.2 and 37.8 °C is shown below.

Temperature, °C	Vapor Pressure kPa	mbar	mmHg = torr
−87.2	6.11	61.1	45.8
−73.7	16.53	165.3	124.0
−45.6	80.49	804.9	603.7
−17.8	266.5	2 665	1 999.1
10.0	680.7	6 807	5 105.6
37.8	1 452.0	14 520	10 891

For additional vapor pressure values, see Table 1 and Figure 3.

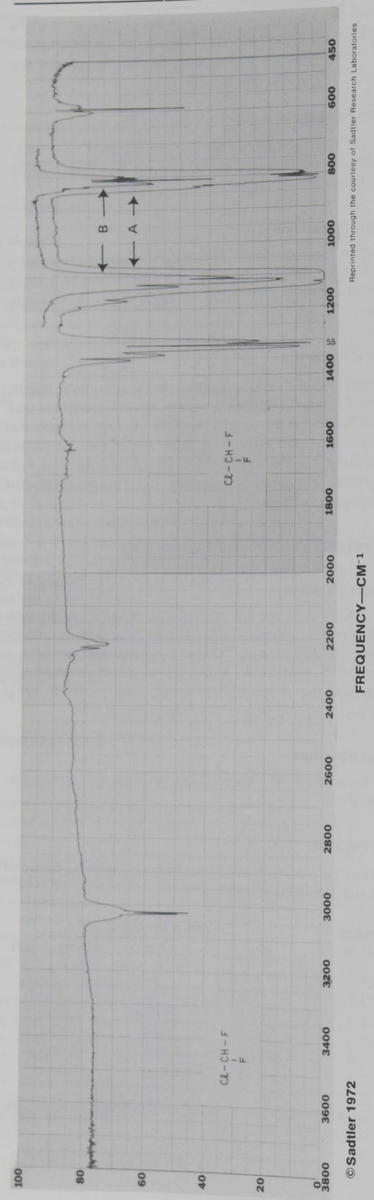


Fig. 2. Infrared spectrum of gaseous $CHClF_2$ in the frequency range 3 800–450 cm^{-1}; 10 cm path length cell, with KBr windows; pressure: curve A: 2.67 kPa (20 mmHg), curve B (partial scan): 0.067 kPa (0.5 mmHg) (5).

Thermodynamic Data

The thermodynamic properties of saturated $CHClF_2$ liquid and vapor are shown in Table 1, while those for the superheated vapor are shown in Table 2.

Thermodynamic Properties of Chlorodifluoromethane as Ideal Gas @ 25 °C (3)

Heat Capacity, C_p°	57.124 J/(mol·°K)
	0.661 kJ/(kg·°K)
Entropy, S°	280.855 J/(mol·°K)
	3.248 kJ/(kg·°K)
Free Energy Function, $(F^\circ_{298} - H^\circ_{298})/T$	−280.855 J/(mol·°K)
	−3.248 kJ/(kg·°K)
Enthalpy, H°	12.414 kJ/mol
	0.144 kJ/kg
Enthalpy of Formation, ΔH_f°	−481.578 kJ/mol
	−5.569 kJ/kg
Free Energy of Formation, ΔF_f°	−450.483 kJ/mol
	−5.210 kJ/kg

REFERENCES

[1] For entensive tabulations of thermodynamic and physical properties of chlorodifluoromethane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, **Effects of Exposure to Toxic Gases**—*First Aid and Medical Treatment*, 2nd edition *1977*, pp. 119–123, Matheson, Lyndhurst, New Jersey.

[3] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRD—NBS 37, U. S. Government Printing Office, Washington, D.C.

[4] *Freon-22 Tech. Bull. T-22, 1964*, E. I. duPont de Nemours & Co., Wilmington, Delaware.

[5] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED $CHClF_2$ LIQUID AND VAPOR (4)

Temperature		Pressure		Entropy kJ/(kg·°K)		Enthalpy kJ/kg		Latent Heat of Vaporization kJ/kg	Specific Volume dm^3/kg		Density kg/dm^3	
°C	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
−101.1	−150	1.873	0.018 5	−0.299	1.234	−60.375	203.437	263.812	0.635 5	8 817	1.574	0.000 113
−75.6	−140	3.081	0.030 4	−0.269	1.202	−55.147	206.134	261.281	0.641 2	5 527	1.560	0.000 181
−90.0	−130	4.899	0.048 4	−0.240	1.173	−49.889	208.846	258.735	0.647 1	3 581	1.545	0.000 279
−84.4	−120	7.552	0.074 5	−0.212	1.146	−44.594	211.570	256.164	0.653 1	2 390	1.531	0.000 418
−78.9	−110	11.319	0.111 7	−0.184	1.122	−39.250	214.304	253.554	0.659 3	1 638	1.517	0.000 610
−73.3	−100	16.536	0.163 2	−0.156	1.099	−33.853	217.035	250.888	0.665 7	1 151	1.502	0.000 869
−67.8	−90	23.600	0.232 9	−0.129	1.079	−28.395	219.762	248.157	0.672 4	826.2	1.487	0.001 21
−62.2	−80	32.972	0.325 4	−0.103	1.060	−22.868	222.472	245.340	0.679 3	605.2	1.472	0.001 65
−56.7	−70	45.176	0.445 8	−0.077	1.043	−17.268	225.164	242.432	0.686 4	451.5	1.457	0.002 22
−51.1	−60	60.798	0.600 0	−0.051	1.027	−11.592	227.828	239.420	0.693 8	342.4	1.441	0.002 92
−45.6	−50	80.489	0.794 4	−0.025	1.013	−5.837	230.454	236.291	0.701 4	263.6	1.426	0.003 79
−40.0	−40	104.952	1.036	0.000	0.999	0.000	233.041	233.041	0.709 4	205.7	1.410	0.004 86
−34.4	−30	134.951	1.332	0.025	0.987	5.920	235.577	229.657	0.717 6	162.6	1.394	0.006 15
−28.9	−20	171.300	1.691	0.050	0.976	11.927	238.058	226.131	0.726 3	130.0	1.377	0.007 69
−23.3	−10	214.854	2.120	0.074	0.965	18.017	240.475	222.458	0.735 3	105.0	1.360	0.009 52
−17.8	0	266.531	2.630	0.099	0.955	24.195	242.823	218.628	0.744 8	85.67	1.343	0.011 67
−12.2	10	327.253	3.230	0.123	0.945	30.459	245.094	214.635	0.754 6	70.48	1.325	0.014 19
−6.7	20	398.014	3.928	0.147	0.936	36.812	247.281	210.469	0.765 0	58.45	1.307	0.017 11
−1.1	30	479.813	4.735	0.170	0.928	43.256	249.375	206.119	0.776 0	48.82	1.288	0.020 48
4.4	40	573.685	5.662	0.194	0.920	49.794	251.370	201.576	0.787 7	41.05	1.269	0.024 36
10.0	50	680.699	6.718	0.217	0.912	56.426	253.255	196.829	0.800 0	34.71	1.250	0.028 81
15.6	60	801.929	7.914	0.240	0.905	63.160	255.019	191.859	0.813 1	29.51	1.230	0.033 89
21.1	70	938.583	9.263	0.263	0.898	70.003	256.651	186.648	0.827 2	25.20	1.209	0.039 68
26.7	80	1 091.65	10.77	0.286	0.891	76.960	258.134	181.174	0.842 3	21.61	1.187	0.046 27
32.2	90	1 262.36	12.46	0.309	0.884	84.047	259.452	175.405	0.858 6	18.60	1.165	0.053 77
37.8	100	1 452.04	14.33	0.332	0.877	91.274	260.581	169.307	0.876 4	16.04	1.141	0.062 32
43.3	110	1 661.91	16.40	0.355	0.870	98.663	261.495	162.832	0.895 8	13.87	1.116	0.072 08
48.9	120	1 893.30	18.68	0.378	0.862	106.238	262.155	155.917	0.917 3	12.01	1.090	0.083 26
54.4	130	2 147.72	21.20	0.402	0.855	114.035	262.513	148.478	0.941 4	10.40	1.062	0.096 14
60.0	140	2 426.54	23.95	0.425	0.847	122.098	262.501	140.403	0.969	9.00	1.032	0.111 10
65.6	150	2 731.63	26.96	0.449	0.838	130.501	262.029	131.528	1.000	7.77	1.000	0.128 68
71.1	160	3 064.93	30.25	0.474	0.827	139.346	260.949	121.603	1.038	6.68	0.963	0.149 69
76.7	170	3 428.49	33.84	0.500	0.815	148.808	259.031	110.223	1.084	5.70	0.922	0.175 49
82.2	180	3 825.07	37.75	0.529	0.800	159.219	255.846	96.627	1.144	4.79	0.874	0.208 60
87.8	190	4 258.13	42.02	0.561	0.780	171.337	250.421	79.084	1.232	3.92	0.812	0.254 92
93.3	200	4 732.28	46.70	0.605	0.744	187.959	239.076	51.117	1.401	2.96	0.714	0.337 67
96.0	204.81	4 977.39	49.12	0.670	0.670	212.289	212.289	0.000	1.905 6	1.905 6	0.524 8	0.524 77

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED $CHClF_2$ VAPOR (4)

M, ENTHALPY, kJ/kg; **S**, ENTROPY, kJ/(kg.°K); **V**, SPECIFIC VOLUME, dm^3/kg

kPa		Temperature, °C								
		−17.8	10.0	37.8	65.6	93.3	148.9	176.7	204.4	232.2
3.4	H	248.745	265.767	283.675	302.447					
	S	1.424	1.487	1.547	1.605					
	V	7 117	7 893	8 668	9 443					
34.4	H	248.099	265.258	283.272	302.124	321.788	341.760			
	S	1.166	1.230	1.290	1.349	1.404	1.354			
	V	236.1	263.9	291.3	318.4	345.2	372.0			
207	H	244.243	262.339	280.997	300.304	320.301	340.998			
	S	0.983	1.050	1.113	1.173	1.229	1.284			
	V	112.4	126.8	140.7	154.4	167.8	181.2			
345	H		259.872	279.107	298.811	319.090	339.991	361.536		
	S		0.995	1.060	1.120	1.178	1.233	1.286		
	V		74.02	82.85	91.36	99.67	107.8	115.9		
689	H			274.077	294.911	315.963	337.418	359.370	381.866	
	S			0.981	1.045	1.105	1.162	1.215	1.267	
	V			39.33	44.04	48.51	52.83	57.04	61.18	
1 379	H			262.081	286.215	309.230	331.990	354.868	378.042	401.614
	S			0.886	0.960	1.025	1.085	1.141	1.194	1.245
	V			17.20	20.22	22.85	25.28	27.59	29.81	31.97
2 068	H				275.695	301.675	326.128	350.109	374.063	398.209
	S				0.897	0.971	1.035	1.094	1.149	1.201
	V				12.06	14.21	16.06	17.75	19.34	20.87

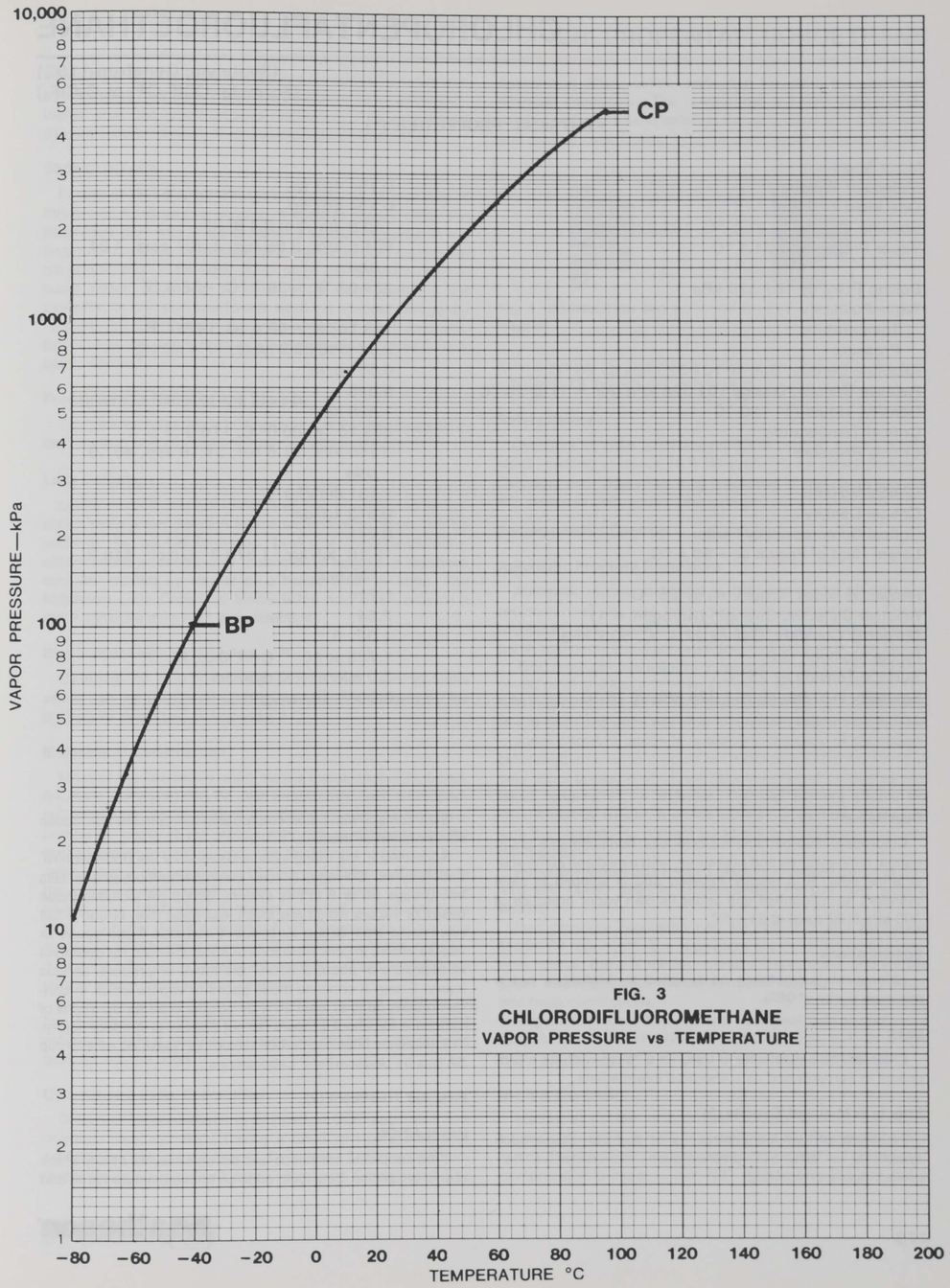


FIG. 3
CHLORODIFLUOROMETHANE
VAPOR PRESSURE vs TEMPERATURE

CHLOROPENTAFLUOROETHANE

(Synonym: Genetron-115®)
(Formula: $CClF_2CF_3$ or C_2ClF_5)

PHYSICAL PROPERTIES (1)

Molar Mass	0.154 467 kg
Molecular Weight	0.154 467 kg
One Mole of C_2ClF_5	149.8 dm^3/kg; 2.4 ft^3/lb
Specific Volume @ 21.1 °C, 101.325 kPa	804.6 kPa; 8.05 bar; 116.7 psia; 7.94 atm
Vapor Pressure @ 21.1 °C	234.03 °K; −39.1 °C; −38.4 °F
Boiling Point @ 101.325 kPa	
Triple Point	
Temperature	173.70 °K; −99.4 °C; 147.0 °F
Pressure	2.32 kPa; 23.2 mbar; 17.4 mmHg
Absolute Density, Gas @ 101.325 kpa @ 20 °C	6.68 kg/m^3
Relative Density, Gas @ 101.325 kPa (Air = 1) @ 20 °C	5.545
Density, Liquid @ −20 °C	1.526 kg/l
Critical Temperature	353.15 °K; 80.0 °C; 176.0 °F
Critical Pressure	3 160 kPa; 31.6 bar; 31.16 atm; 457.9 psia
Critical Volume	1.631 dm^3/kg
Critical Density	0.613 kg/dm^3
Critical Compressibility Factor	0.271
Latent Heat of Fusion @ −99.4 °C	12.16 kJ/kg; 1 878.2 J/mol; 448.9 cal/mol
Refractive Index, Liquid, n_D @ 25 °C	1.214
Relative Dielectric Strength (Nitrogen = 1)	2.54
Dielectric Constant, Gas @ 27.4 °C, 50.7 kPa	1.001 8
Dipole Moment, Gas	1.735×10^{-30} C·m; 0.52 D
Surface Tension @ 25 °C	7.0 mN/m; 7.0 dyn/cm
Solubility in Water @ 101.325 kPa @ 25 °C	0.006% (by weight)

Description

Chloropentafluoroethane is a colorless, nonflammable gas at normal temperatures and pressures, with a mild and somewhat ethereal odor. It is readily liquefied and is shipped in steel cylinders as a liquefied gas under its own vapor pressure of 703 kPa (102 psig) at 21.1 °C.

Specifications

Chloropentafluoroethane as supplied by Matheson has a minimum purity of 98%.

Uses

Chloropentafluoroethane is used as a refrigerant, as a propellant in aerosols and as a chemical intermediate.

Effects in Man and Toxicity (2)

Inhalation of high concentrations of gas can cause such symptoms as dizziness, disorientation, incoordination, narcosis, nausea or vomiting.

Skin contact with liquid chloropentafluoroethane can cause skin irritation or frostbite.

According to the rating system devised by the Underwriters' Laboratories, Chicago, Illinois, chloropentafluoroethane falls into groups 5A or 6 in this system. Group 5A includes those gases or vapors which are much less toxic than Group 4 but more toxic than Group 6. Group 4 includes those gases or vapors which, in concentrations of about 2–2.5% for durations of exposure of about 2 hours, are lethal or produce serious injury. Group 6 contains those gases or vapors which in concentrations up to at least 20% by volume in air for durations of exposure for about 2 hours do not appear to produce injury. The relatively nontoxic carbon dioxide is classified as a Group 5A gas by Underwriters' Laboratories.

First Aid Treatment (2)

INHALATION

If the subject is conscious and becomes aware of any of the above symptoms, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration if necessary and oxygen simultaneously. Treat symptomatically thereafter.

SKIN CONTACT

In case of skin contact with the low boiling liquid members of this group, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed in the handling and storage of chloropentafluoroethane.

Leak Detection

Leaks of chloropentafluoroethane may be detected by applying soap water solution to suspected points; leaks will be indicated by bubble formation. Leaks of chloropentafluoroethane in dark, confined or inaccessible spaces or locations may be located by means of a halide torch or lamp. The Matheson Leak Detectors Model 8016 and 8017 provide a more sensitive means of leak detection.

Disposal of Leaking Cylinders

Cylinders of chloropentafluoroethane that develop leaks which can not readily be corrected should be handled by the procedure described in Appendix II-C.

Materials of Construction

Most of the commonly used metals (steel, cast iron, brass, tin, lead, aluminum) may be used satisfactorily with chloropentafluoroethane under normal conditions of use. At high temperatures, some of the metals may act as catalysts for the breakdown of the compound. The tendency of metals to promote thermal decomposition of chloropentafluoroethane is in the following approximate order: silver > brass > bronze > aluminum > 1340 steel > copper > nickel > 18-8 stainless steel > inconel (least decomposition). Magnesium alloys and aluminum containing more than 2% magnesium are not recommended for use in systems containing chloropentafluoroethane where water may be present.

In general, gasket materials should not contain natural rubber. Neoprene, or Isoprene rubber, pressed fibers, including asbestos, with a number of insoluble binders, and metallic gaskets may be used.

Cylinder and Valve Description

Chloropentafluoroethane is shipped in DOT approved, low pressure steel cylinders, having a rated service pressure of 1 550 kPa (225 psig) or more. Cylinders of chloropentafluoroethane are equipped with brass valves with Compressed Gas Association (CGA) outlet connection No. 660, the approved alternate connection. The valve outlet is 1.030 inches in diameter, with right-hand external threads, used with a flat seat and washer (see Figure 1 for an illustration). Lecture bottles have a special 5/16 inch-32 threads per inch female outlet and a 9/16 inch-18 threads per inch male dual valve outlet.

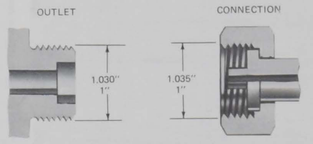


Fig. 1. CONNECTION 660 1.030″-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders of chloropentafluoroethane contain fusible metal plugs, melting at about 73.9 °C (165 °F) as safety devices. Cylinders over 30 inches long (exclusive of the neck) require this device in both ends of the cylinder.

Recommended Controls

Automatic Pressure Regulators

Automatic regulators Model 1L-660 and Model 1P-660 are recommended for use with chloropentafluoroethane. These regulators are constructed of a brass body, brass internal parts, and neoprene diaphragm and neoprene seat. The Model 1L-660 regulator has a delivery pressure range of 28–550 kPa (4–80 psig) and has a cylinder pressure gauge. The Model 1P-660 regulator has a delivery pressure range of 28–240 kPa (4–35 psig) and does not have a cylinder pressure gauge. No cylinder pressure gauge is required in the case of chloropentafluoroethane, since it would not indicate cylinder content but only vapor pressure which will remain constant as long as any liquid remains in the cylinder. Cylinder content should be determined by weight. A check valve is recommended for use with the regulator to prevent suckback of foreign material into the regulator.

Regulator Model 3321 with a delivery pressure range of 28–410 kPa (4–60 psig) is recommended for use with lecture bottles.

Low pressure regulation can be obtained with Matheson Model 70 regulators. The regulators are constructed of aluminum bodies, Buna N rubber oversize diaphragms, and rubber seats. The regulators have brass needle valves, ¼″ NPT male, and hose connections.

Regulator Models 70B, 70 and 70A have delivery pressure ranges of 0.5–3.0 kPa (2–12″ water column), 3.4–34.5 kPa (0.5–5 psig), and 34.5–69 kPa (5–10 psig), respectively.

Manual Controls

Matheson needle valve Model 50-660, a brass bar stock valve, is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets (¼″ compression fitting or ¼ inch NPT male or female pipe), but is

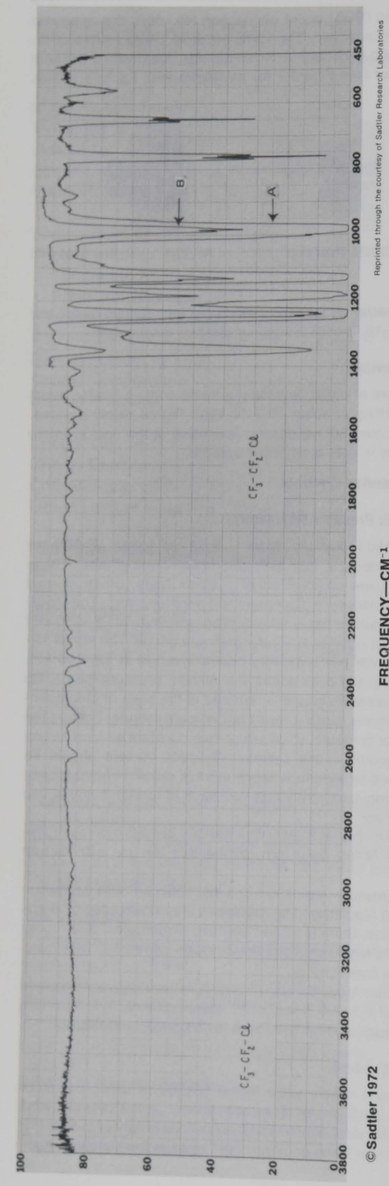


Fig. 2. Infrared spectrum of gaseous C_2ClF_5 in the spectral region 3 800–450 cm^{-1}; 10 cm path length cell, with KBr windows; pressure: curve A: 2.666 kPa (20 mmHg); curve B (partial scan): 0.006 7 kPa (0.05 mmHg (3).

usually supplied with a serrated hose end. It should be used only where manual flow control is needed and should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. A Model 31B manual needle valve is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure or temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Commercial Preparations

A number of fluorination procedures are described for the preparation of chloropentafluoroethane; generally, other fluorocarbons are also formed: (1) fluorination of 1,1,1-trichloro-2,2,2-trichloroethane with hydrogen fluoride at 450 °C over aluminum fluoride catalysts: (2) fluorination of 1,1,2-trifluoroethane with hydrogen fluoride at 346 °C over aluminum fluoride catalyst; (3) passage of perchloroethylene, chlorine, and hydrogen fluoride over aluminum trifluoride.

Chemical Properties

Chloropentafluoroethane is chemically stable, does not decompose at high temperatures, and does not attack metals except at elevated temperatures.

Shipping Regulations

Chloropentafluoroethane is shipped in steel cylinders as a nonflammable, compressed gas, taking a nonflammable DOT Label.

See Tables 1 and 2 for thermodynamic properties of the saturated liquid and superheated vapor, respectively.

Thermodynamic and Detailed Physical Data

Entropy, Ideal Gas
@ −39.1 °C 331.71 J/(mol·°K)
79.28 cal/(mol·°K)

Entropy, Ideal Gas
@ 25 °C 357.73 J/(mol·°K)
85.5 cal/(mol·°K)

Entropy, Liquid @ −39.1 °C 248.03 J/(mol·°K)
59.28 cal/(mol·°K)

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous chloropentafluoroethane.

Vapor Pressure (4)

The vapor pressure of liquid C_2ClF_5 from the triple point (173.70 °K) to the boiling point (234.03 °K) is expressed by the following equation:

$$\log_{10}p = 36.185\,941 - \frac{1\,823.225}{T} - 11.510\,21\log_{10}T + 0.007\,503\,762T$$

in which p = mmHg, and T = °K.

Some vapor pressure values calculated by this equation are tabulated below.

Temperature, °K	Vapor Pressure kPa	Vapor Pressure mbar	Vapor Pressure mmHg = torr
177.838	3.125	31.25	23.44
182.830	4.72	47.2	35.40
190.728	8.60	86.0	64.53
208.066	26.69	266.9	200.22
217.131	44.37	443.7	332.80
225.342	67.47	674.7	506.08
233.303	98.04	980.4	735.34
233.925	100.82	1 008.2	756.18

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv	
Temperature, °K	ΔHv, kJ/kg
193.15	140.46
213.15	132.47
234.03	125.65
253.15	119.37
273.15	110.58

REFERENCES

[1] For extensive tabulations of thermodynamic and physical properites of chloropentafluoroethane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 119–123, Matheson, Lyndhurst, New Jersey.

[3] *The Sadtler Standard Spectra*, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[4] J. G. Aston, P. E. Wills, and T. P. Zolki, *J. Amer. Chem. Soc.* 77, 3939 (1955).

[5] *Thermodynamic Properties of Monochloropentafluoroethane, Tech. Bull. T-115, 1958*, E. I. duPont de Nemours & Co., Wilmington, Delaware.

Table 1. THERMODYNAMIC PROPERTIES OF THE SATURATED LIQUID AND VAPOR (5)

Temperature		Pressure		Entropy J/(kg•K)	Enthalpy kJ/kg		Latent Heat of Vaporization	Specific Volume dm^3/kg		Density kg/dm^3	
°K	°F	kPa	atm	vapor	Liquid	Vapor	kJ/kg	Liquid	Vapor	Liquid	Vapor
177.59	−140	3.040	0.030	564.129	−49.185	93.654	142.839	0.579	3 083.9	1.727	0.000 32
188.71	−120	7.412	0.073	551.744	−39.722	99.965	139.687	0.590	1 362.8	1.695	0.000 73
199.82	−100	15.892	0.157	544.297	−30.127	106.434	136.561	0.602	670.10	1.661	0.001 49
210.93	−80	31.088	0.307	540.782	−20.346	113.026	133.372	0.615	359.34	1.626	0.002 78
222.04	−60	56.330	0.556	540.322	−10.316	119.707	130.023	0.629	206.82	1.590	0.004 84
233.15	−40	95.669	0.944	542.246	0.000	126.436	126.436	0.644	126.17	1.553	0.007 93
244.26	−20	154.098	1.521	545.970	10.639	133.165	122.526	0.660	80.73	1.515	0.012 39
255.37	0	236.973	2.339	551.075	21.636	139.846	118.210	0.679	53.71	1.473	0.018 62
266.48	20	350.323	3.457	557.016	33.012	146.414	113.402	0.699	36.88	1.431	0.027 12
277.59	40	500.766	4.942	563.208	44.801	152.800	107.999	0.722	25.98	1.385	0.038 49
288.71	60	694.99	6.86	569.986	57.051	158.911	101.860	0.749	18.65	1.335	0.053 62
299.82	80	941.82	9.30	576.137	69.826	164.626	94.800	0.780	13.57	1.282	0.073 69
310.93	100	1 247.95	12.32	581.367	83.236	169.770	86.534	0.818	9.94	1.222	0.100 6
322.04	120	1 623.03	16.02	584.840	97.459	174.059	76.600	0.868	7.27	1.152	0.137 6
333.15	140	2 076.70	20.50	585.174	112.845	176.967	64.122	0.938	5.25	1.066	0.190 5
344.26	160	2 620.01	25.86	578.856	130.329	177.192	46.863	1.061	3.62	0.943	0.276 2
349.82	170	2 928.89	28.91	569.652	141.154	175.003	33.849	1.196	2.87	0.836	0.348 4
353.09	175.89	3 123.32	30.82	521.285	158.450	158.450	0.000	1.677 4	1.677 4	0.596 2	0.596 2

Matheson

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED C_2C1F_5 VAPOR (5)

H, ENTHALPY, kJ/kg; **S**, ENTROPY, J/(kg·°K); **V**, SPECIFIC VOLUME, dm^3/kg

PRESSURE kPa	atm		TEMPERATURE, °K 188.71	210.93	233.15	255.37	277.59	299.82	322.04	344.26	366.48	388.71	410.93	422.04
		H	100.044	113.433	127.635	142.581	158.225	174.542	191.464	208.968	226.982	245.508	264.452	274.075
3.447	0.034	S	592.873	659.398	724.250	785.337	843.913	900.815	954.789	1 007.507	1 057.715	1 107.086	1 155.621	1 178.214
		V	2 937	2 825	3 633	3 980	4 328	4 675	5 022	5 368	5 715	6 062	6 411	6 580
		H	99.974	113.386	127.589	142.535	158.178	174.473	191.418	208.921	226.935	245.485	264.406	274.052
6.895	0.068	S	555.635	622.579	687.013	748.099	806.675	863.159	917.970	970.270	1 020.896	1 069.430	1 117.546	1 140.140
		V	1 465	1 640	1 814	1 988	2 162	2 335	2 509	2 683	2 857	3 030	3 204	3 291
		H		113.177	127.403	142.372	158.016	174.287	191.278	208.805	226.796	245.345	264.313	273.982
20.684	0.204	S		563.166	627.182	688.268	747.262	804.165	858.557	911.275	961.483	1 010.854	1 058.134	1 081.146
		V		542.9	601.5	659.9	718.5	776.6	834.7	892.7	950.8	1 009	1 067	1 096
		H			127.147	142.233	157.899	174.217	191.162	208.712	226.703	245.229	264.220	273.866
41.369	0.408	S			589.107	650.612	709.188	766.509	820.901	873.619	924.246	973.198	1 020.896	1 043.490
		V			298.4	331.2	357.4	386.7	416.0	445.2	474.5	503.6	532.7	547.2
		H			126.961	141.977	157.853	174.171	191.093	208.642	226.633	245.182	264.150	273.820
55.158	0.544	S			572.790	634.713	693.707	750.610	805.420	857.720	908.765	957.299	1 004.997	1 028.009
		V			222.6	244.9	267.2	289.3	311.4	333.4	355.3	377.3	399.2	410.1
		H			126.798	141.814	157.690	174.054	190.976	208.572	226.564	245.113	264.103	273.750
68.948	0.680	S			560.656	622.161	681.155	738.476	793.286	845.586	896.631	945.584	992.863	1 015.875
		V			177.1	195.1	213.0	230.8	248.5	266.3	283.9	301.5	319.0	327.7
		H				141.349	157.225	173.682	190.651	208.224	226.378	244.834	263.917	273.587
103.421	1.021	S				599.567	658.980	716.301	770.693	823.411	874.038	923.827	970.688	993.700
		V				128.7	140.8	152.9	164.8	176.7	188.6	200.4	212.2	218.1
		H				140.954	156.923	173.404	190.325	208.014	226.192	244.694	263.801	273.378
137.895	1.361	S				583.250	642.662	699.983	754.375	807.094	858.138	907.510	954.789	978.219
		V				95.5	104.8	113.9	122.9	132.0	141.0	149.8	158.8	163.2
		H				140.187	156.226	172.776	189.930	207.526	225.750	244.299	263.406	272.959
206.843	2.041	S				559.401	619.232	676.553	731.363	784.500	835.545	899.560	932.195	956.044
		V				62.2	68.6	74.9	81.1	87.2	93.3	99.3	105.3	108.3
		H					155.482	172.195	189.396	206.992	225.215	243.904	263.104	272.657
275.790	2.722	S					601.659	664.001	714.627	768.182	819.227	868.598	916.296	940.145
		V					50.5	55.3	60.1	64.8	69.5	74.0	78.6	80.9
		H					153.994	170.777	188.094	205.969	224.286	243.137	262.128	271.937
413.685	4.083	S					576.137	634.713	690.360	743.915	795.797	845.586	893.702	916.714
		V					32.3	35.8	39.1	42.4	45.6	48.8	51.9	53.5
		H						169.243	186.769	204.830	223.333	242.207	261.314	271.123
551.581	5.444	S						615.885	672.369	726.761	778.224	828.432	876.548	899.560
		V						26.0	28.6	31.2	33.7	36.1	38.5	39.8

Matheson

Table 2—*Continued*

PRESSURE kPa	PRESSURE atm		TEMPERATURE, °K 188.71	210.93	233.15	255.37	277.59	299.82	322.04	344.26	366.48	388.71	410.93	422.04
689.476	6.805	H						167.778	185.421	203.807	222.310	241.277	260.570	270.403
		S						600.404	657.725	712.117	764.835	814.625	863.159	886.171
		V						20.0	22.3	24.4	26.5	28.5	30.5	31.5
1 034.214	10.21	H							182.027	200.809	219.706	238.930	258.664	268.404
		S							627.600	684.084	737.639	788.266	837.637	861.067
		V							13.8	15.4	17.0	18.4	19.9	20.5
1 378.951	13.61	H							177.773	531	217.010	236.535	256.526	266.544
		S							602.496	072	716.719	768.601	817.972	842.239
		V							9.38		12.1	13.4	14.5	15.1
1 723.689	17.01	H								487	214.035	234.095	254.108	264.452
		S								173	698.310	751.446	802.073	826.758
		V									9.21	10.3	12.0	12.3
2 068.427	20.41	H								373	210.455	231.282	251.784	262.174
		S								487	681.155	735.966	787.847	812.533
		V									7.25	8.25	9.13	9.55
2 757.903	27.22	H									201.948	224.936	246.972	257.688
		S									648.520	709.188	762.743	789.102
		V									4.67	5.64	6.44	6.81
3 123.325	30.82	H									196.601	221.450	241.765	255.084
		S									629.274	695.381	751.446	778.224
		V									3.71	4.72	5.49	5.84
3 447.378	34.02	H									191.139	218.172	241.091	252.528
		S									604.588	681.992	741.405	769.438
		V									3.03	4.05	4.82	5.15

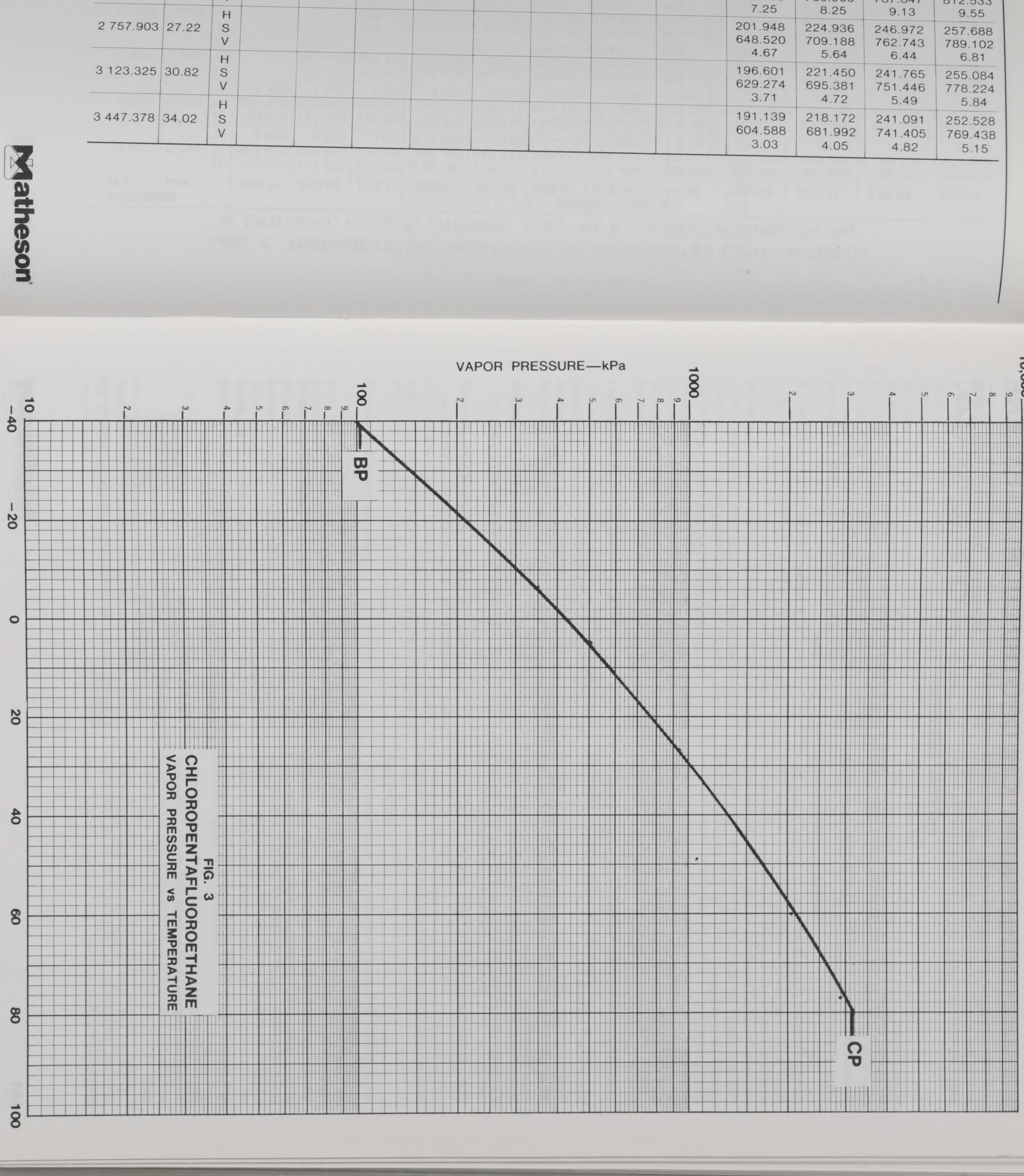


FIG. 3
CHLOROPENTAFLUOROETHANE
VAPOR PRESSURE vs TEMPERATURE

Matheson®

CHLOROTRIFLUOROETHYLENE

(Synonym: Genetron-1113®, CTFE)
(Formula: $CF_2=CClF$ or C_2ClF_3)

PHYSICAL PROPERTIES (1)

Molar Mass	0.116 470 kg
Molecular Weight	0.116 470 kg
One Mole of C_2ClF_3	206 dm^3/kg; 3.3 ft^3/lb
Specific Volume @ 21.1 °C, 101.325 kPa	528.8 kPa; 5.29 bar; 76.7 psia; 5.22 atm
Vapor Pressure @ 21.1 °C	244.79 °K; -28.4 °C; -19.0 °F
Boiling Point @ 101.325 kPa	114.99 °K; -158.2 °C; -252.7 °F
Melting Point @ 101.325 kPa	4.976 kg/m^3
Absolute Density, Gas @ 20 °C	4.13
Relative Density, Gas @ 20 °C, 101.325 kPa (Air = 1)	1.467 kg/l
Density, Liquid @ -40 °C	378.95 °K; 105.8 °C; 222.4 °F
Critical Temperature	4 063 kPa; 40.63 bar; 589.3 psia; 40.1 atm
Critical Pressure	1.82 dm^3/kg
Critical Volume	0.550 kg/dm^3
Critical Density	0.273
Critical Compressibility Factor	47.67 kJ/kg; 5 552.6 J/mol; 1 327.1 cal/mol
Latent Heat of Fusion @ -158.2 °C	8.4–38.7% (by volume)
Flammable Limits in Air	2.03 × 10^{-30} C.m; 0.61 D
Dipole Moment, Gas	85.994 J (mol·°K)
Molar Specific Heat, Gas @ 25 °C, 101.325 kPa @ Constant Pressure	122.424 J/(mol·°K)
Molar Specific Heat, Liquid @ -28.4 °C	0.013 2 mPa·s 0.013 2 $mN·s/m^2$; 0.013 2 cP
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.010 62 W/(m·°K); 25.4 × 10^{-6} cal·cm/s cm^2·°C)
Thermal Conductivity @ 101.325 kPa @ 20 °C	

Description

Chlorotrifluoroethylene (CTFE) is a flammable, colorless gas at room temperature and pressure with a faint ethereal odor. It is very reactive and must be stabilized with an inhibitor, tributylamine. As shipped, it contains 1.0% by weight of the inhibitor. It is shipped in steel cylinders as a liquefied gas under its own vapor pressure of 430 kPa (62 psig) at 21.1 °C.

Specifications

CTFE has a minimum purity of 99.0%.

Uses

CTFE has been used in polymerization reactions and as a chemical intermediate. It is the monomer of an inert plastic known as Kel-F.®

Effects In Man and Toxicity (2)

Limited experience with animals indicates that exposure to high concentrations of vapors of CTFE may produce pulmonary damage, irritation and edema. Contact with the liquid state of CTFE may produce frostbite.

No quantitative toxicity data are available for CTFE. Based on animal experiments, CTFE is considered to be comparatively of moderate toxicity.

First Aid Treatment (2)

Inhalation

Remove the victim to an uncontaminated atmosphere, administer oxygen, and observe for premonitory signs of delayed pulmonary edema. Subsequent treatment is symptomatic and supportive.

Skin Contact

In case of skin contact with liquid CTFE, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42°C (108 °F). If warm water is not available or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The hazards involved in the handling and use of CTFE are due to its flammability and toxicity. Store and use CTFE cylinders in well-ventilated areas away from heat and all sources of ignition such as flames and sparks. Never use flames to detect CTFE leaks; use soapy water. Do not use CTFE around sparking motors or other non-explosionproof equipment. Do not store reserve stocks of CTFE cylinders containing oxygen, chlorine or other highly oxidizing or flammable materials. Ground all lines and equipment containing CTFE. In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Never use a flame to detect CTFE leaks, use soapy water. Leaks will be evident by the formation of bubbles. A halide leak detector has been used satisfactorily in the detection of CTFE leaks and for monitoring an area for long-term exposure.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-A.

Materials of Construction

Since CTFE is non-corrosive, no special materials of construction are required, provided the system is dry. However, any piping and vessels should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

CTFE is shipped in DOT approved low pressure steel cylinders. The assigned standard cylinder valve outlet is Compressed Gas Association (CGA) connection No. 510. The approved alternate connection is the CGA No. 660. The valve is of brass construction having an outlet of thread size 1.030 inches diameter with right-hand external threads, with a connector having a flat seat and washer. (See Figure 1 for an illustration of this cylinder valve outlet and its mating connection).

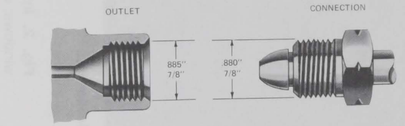


Fig. 1. CONNECTION 510 .885″-14 LH INT. accepting a Bullet Shaped Nipple

Lecture bottles have a special 5/16″-32 threads per inch female valve outlet and a 9/16″-18 threads per inch male dual valve outlet.

Safety Devices

CTFE cylinders have a safety device of the fusible metal type, melting at approximately 73.9 °C (165 °F).

Recommended Controls

Automatic Pressure Regulator

Matheson supplies single stage regulator Model 1P-660 for CTFE service. The regulator has a brass body, with brass internal parts, neoprene diaphragm, and neoprene seat. It has a delivery pressure range of 28-240 kPa (4-35 psig). No cylinder pressure gauge is necessary in this regulator since it would not indicate cylinder content but only vapor pressure which will remain constant as long as any liquid remains in the cylinder. Cylinder content should be determined by weighing.

Matheson regulator Model 70-660 will provide accurate low pressure regulation in the delivery pressure range of 3.4-34.5 kPa (0.5-5.0 psig). This regulator has an oversize pancake body of die cast aluminum with a Buna N diaphragm.

A check valve is recommended for use with either regulator to prevent suckback of foreign materials.

Manual Controls

Matheson needle valve Model 50-660, a brass bar stock valve, is available for direct connection to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, ¼″ NPT male or female pipe. It is used for intermittent flow control directly from the cylinder, but it requires constant attention by the user. It should not be used as a pressure control since dangerous pressures can develop if a line or the system itself becomes clogged. Needle valve Model 31B is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and the one from the potentiometer are compared. If

there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

CTFE is shipped under DOT regulations as a flammable, liquefied compressed gas, taking a "Red Gas Label".

Chemical Preparation

CTFE is prepared from 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113®) by dechlorination with zinc in ethyl alcohol.

Chemical Properties

CTFE exhibits typical ethylenic properties.

1. It adds bromine and chlorine directly.
2. It adds fluorine directly at 0 °C or by reaction with antimony pentafluoride at 95 °C.
3. It adds hydrogen bromide and hydrogen chloride readily.
4. It decolorizes potassium permanganate.

It hydrolyzes slowly in contact with water and more rapidly in 10% sodium hydroxide solution at 60 °C. CTFE undergoes further addition and condensation with many other reagents. It undergoes polymerization (for this purpose the inhibitor should be removed) giving a dimer, a low molecular weight polymer, or a high molecular weight polymer depending on the reaction conditions. It may also be copolymerized. The inhibitor may be removed by fractional distillation in a nitrogen atmosphere or by washing with cold dilute hydrochloric acid. Once the inhibitor has been removed, CTFE should be used promptly and kept free from contact with atmospheric oxygen.

Thermodynamic and Detailed Physical Data

Molecular Structure

CTFE has D_{2h} symmetry, a symmetry number of four, and the following bond distances and angles: C—F and C=C: 1.313×10^{-10} m (1.313 Å); F-C-C: 114 °.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous CTFE.

Vapor Pressure (3)

The vapor pressure of liquid CTFE over the temperature range −67.0 °C to −11.0 °C is shown in the following table.

Temperature, °C	Vapor Pressure kPa	mbar	mmHg = torr
−66.8	12.964	129.6	97.24
−52.5	30.820	308.2	231.17
−44.6	46.976	469.8	352.35
−40.7	57.045	570.4	427.87
−37.0	68.450	684.5	513.42
−33.1	81.927	819.3	614.50
−30.3	93.112	931.1	698.40
−28.4	101.408	1 014.1	760.62
−26.5	110.019	1 100.2	825.21
−23.0	127.151	1 271.5	953.71
−19.0	150.174	1 501.7	1 126.4

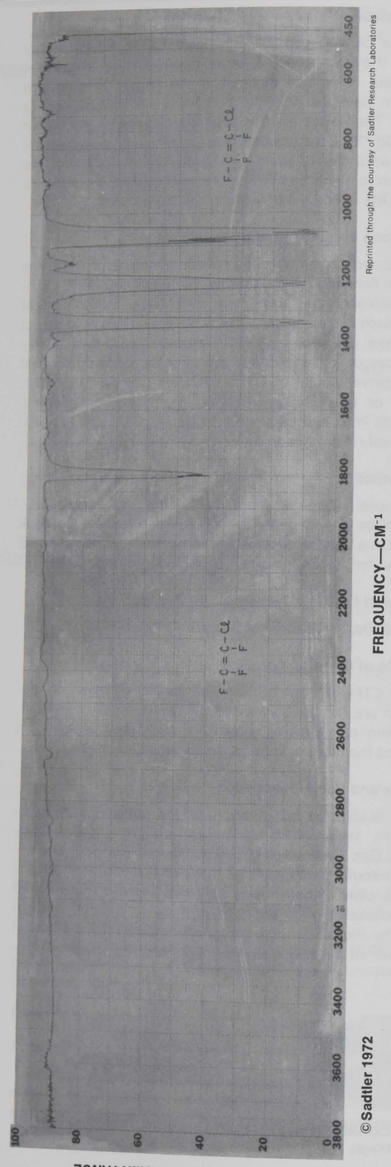


Fig. 2. Infrared spectrum of gaseous C_2ClF_3 over the frequency range 3 800-450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure: 3 kPa (15 mmHg) (7).

Temperature, °C	Vapor Pressure kPa	mbar	mmHg = torr
−15.6	171.629	1 716.3	1 287.3
−10.9	205.410	2 054.1	1 540.7

These data are represented by the following Antoine vapor pressure equation (3):

$$\log_{10} p = 6.901\,99 - \frac{850.649}{t + 239.91}$$

in which p = mmHg and t = °C.

The vapor pressure from the boiling point (−27.9 °C) to the critical point (105.8 °C) is shown below (4);

Temperature, °C	Vapor Pressure kPa	bar
−28.9	101.325	1.013 25
−11.1	202.650	2.03
15.5	506.625	5.07
40.0	1 013.250	10.1
71.1	2 026.500	20.3
91.9	3 039.750	30.4
105.8	4 063 132	40.6

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔH_v Temperature °C	ΔH_v, kJ/mol
−100.0	25.34
−80.0	24.30
−60.0	22.86
−40.0	21.40
−28.4	20.77 (3)
0.0	19.94

Thermodynamic Properties of CTFE as Ideal Gas @ 26.8 °C (5)

Heat Capacity, C_p°	84.167 J/(mol·°K)
Entropy, S°	322.9 J/(mol·°K)
Free Energy Function, $(F_T^\circ - E_0^\circ)/T$	−265.3 J/(mol·°K)
Enthalpy Function, $(H^\circ - E_0^\circ)/T$	57.65 J/mol
Standard Enthalpy of Formation, H_f° (6) @ 25.0 °C	−555.22 kJ/mol
Free Energy of Formation, ΔF_f° (6) @ 25.0 °C	−523.84 kJ/mol
Enthalpy Difference, $H^\circ - H_0^\circ$ (6) @ 25.0 °C	17.138 kJ/mol
Entropy, Ideal Gas, S° @ −28.4 °C	306.19 J/(mol·°K) (3)
@ 25 °C (6)	322.00 J/(mol·°K)
Entropy, Liquid, S (3) @ −28.4 °C	220.66 J/(mol·°K)

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of chlorotrifluoroethylene, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Exposure To Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 103–105, Matheson, Lyndhurst, New Jersey.

[3] G. D. Oliver, J. W. Grisard, and C. W. Cunningham, *J. Amer. Chem. Soc.* 73, 571 (1951).

[4] *Chemical Engineers' Handbook*, R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, editors, 4th edition, *1963*, p. 3–59, McGraw-Hill Book Co., Inc. New York, New York.

[5] D. F. Mann, N. Acquista, and E. K. Plyler, *J. Chem. Phys.* 21, 1949 (1953).

[6] D. D. Wagman, *et al.*, *Selected Values of Chemical Thermodynamic Properties*, Natl. Bur. Stand. Tech. Note 270-3, *1968*, U. S. Government Printing Office, Washington, D. C.

[7] *The Sadtler Standard Spectra*, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

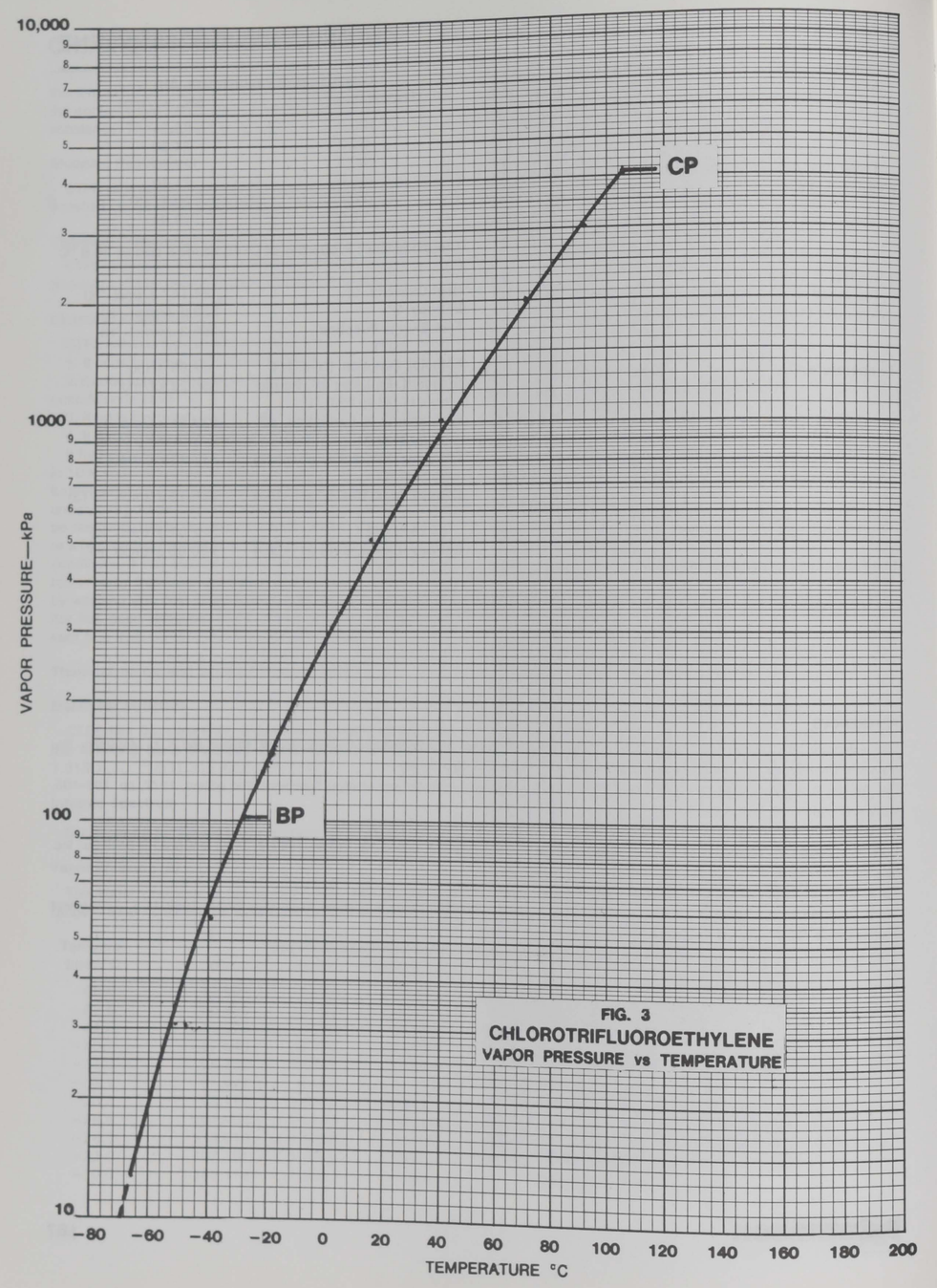


FIG. 3
CHLOROTRIFLUOROETHYLENE
VAPOR PRESSURE vs TEMPERATURE

CHLOROTRIFLUOROMETHANE

(Synonym: Freon-13®, Genetron-13®, Isotron-13®)
(Formula: $CClF_3$)

PHYSICAL PROPERTIES (1)

Molar Mass	0.104 459 kg
Molecular Weight	0.104 459 kg
One Mole of $CClF_3$	218.5 dm^3/kg; 3.5 ft^3/lb
Specific Volume @ 21.1 °C, 101.325 kPa	3 263.9 kPa; 32.64 bar; 473.4 psia; 32.2 atm
Vapor Pressure @ 21.1 °C	191.75 °K; -81.4 °C; -114.5 °F
Boiling Point @ 101.325 kPa	92.15 °K; -181.0 °C; -293.8 °F
Freezing Point In Air @ 101.325 kPa	4.349 kg/m^3
Absolute Density, Gas @ 101.325 kPa, 20 °C	3.61
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	1.347 kg/dm^3
Density, Liquid @ -40 °C	302.0 °K; 28.8 °C; 83.9 °F
Critical Temperature	3870.6 kPa; 38.71 bar; 38.2 atm; 561.4 psia
Critical Pressure	1.730 4 dm^3/kg
Critical Volume	0.578 kg/dm^3
Critical Density	0.279
Critical Compressibility Factor	1.199
Refractive Index, Liquid, n_D @ -73.3 °C	
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	67.655 kJ/(kmol·°K); 67.655 J/(mol·°K); 16.170 cal/(mol·°K)
@ Constant Volume	59.342 kJ/(kmol·°K); 59.342 J/(mol·°K); 14.183 cal/(mol·°C)
Specific Heat Ratio, Gas @ 101.325 kPa, Cp/Cv @ 25 °C	1.140
Molar Specific Heat, Liquid @ -40 °C	104.458 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.014 40 mPa·s; 0.014 40 $mN·s/m^2$; 0.014 40 cP
Viscosity, Liquid @ -40 °C	0.290 mPa·s; 0.290 $mN·s/m^2$; 0.290 cP
Thermal Conductivity, Liquid @ -60 °C	0.088 28 W/(m·°K); 210.994 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ -73.3 °C	17.0 mN/m; 17.0 dyn/cm
Relative Dielectric Strength (Nitrogen = 1)	1.65
Dielectric Constant Gas @ 29.0 °C, 50.7 kPa	1.001 3
Solubility in Water @ 25 °C, 101.325 kPa	0.009% (by weight)

Description

Chlorotrifluoromethane is a colorless, nonflammable, non-corrosive gas. In concentrations up to 20% (by volume), it is odorless; in higher concentrations, it has a mild, ethereal odor similar to that of carbon tetrachloride. It is shipped as a liquefied gas under its own vapor pressure of 3 163 kPa (458 psig) at 21.1 °C.

Specifications

Chlorotrifluoromethane has a minimum purity of 99.0%, the balance being other halocarbons and traces of air.

Uses

Chlorotrifluoromethane is used as a low-temperature refrigerant.

Effects in Man and Toxicity (2)

Inhalation of high concentrations of gaseous chlorotrifluoromethane can cause such symptoms as dizziness, disorientation, incoordination, narcosis, nausea or vomiting. There appear to be no irreversible effects once the oxygen deficiency has been corrected.

Skin contact with liquid chlorotrifluoromethane can cause frostbite.

Chlorotrifluoromethane is classified as a Group 5A or 6 gas according to the rating system devised by the Underwriters' Laboratories, Chicago, Illinois. Group 5A includes those gases or vapors which are much less toxic than Group 4 but more toxic than Group 6. Group 4 includes those gases or vapors which, in concentrations of about 2–2.5% for durations of exposure of about 2 hours, are lethal or produce serious injury. Group 6 contains those gases or vapors which, in concentrations up to at least 20% by volume in air for durations of exposure for about 2 hours, do not appear to produce injury. The relatively nontoxic carbon dioxide is classified as a Group 5A gas by Underwriters' Laboratories.

First Aid Treatment (2)

Inhalation

If the subject is conscious and becomes aware of any of the above symptoms, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration if needed and oxygen simultaneously. Treat symptomatically thereafter.

Skin Contact

In case of skin contact with liquid $CClF_3$, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Leak Detection

Leaks of chlorotrifluoromethane may be detected by applying soap water solution to suspected points; leaks will be indicated by bubble formation. Leaks of chlorotrifluoromethane in dark, confined or inaccessible spaces or locations may be located by means of a halide torch or lamp. The Matheson Model 8016 and 8017 Leak Detector provides a more sensitive means of leak detection.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-C.

Materials of Construction

Most of the commonly used metals (steel, cast iron, brass, copper, tin, lead, aluminum) may be used satisfactorily with chlorotrifluoromethane under normal conditions of use. At high temperatures, some of the metals may act as catalysts for the breakdown of the compound. The tendency of the metals to promote thermal decomposition of chlorotrifluoromethane is in the following approximate order: silver > brass > bronze > aluminum > 1340 steel > copper > nickel > 18-8 stainless steel > inconel (least decomposition). Magnesium alloys and aluminum containing more than 2% magnesium are not recommended for use in systems containing chlorotrifluoromethane where water may be present.

In general, gaskets should not contain natural rubber. Neoprene or Isoprene rubber, pressed fibers, including asbestos, with a number of insoluble binders, and metallic gaskets may be used.

Cylinder and Valve Description

Chlorotrifluoromethane is shipped in DOT approved steel cylinders. Cylinders containing chlorotrifluoromethane are equipped with brass valves with Compressed Gas Association (CGA) outlet connection No. 320, the approved alternate connection. The valve outlet has a thread size of 0.825 inch, with right-hand external threads used with a flat seat and washer (see Figure 1 for an illustration). Lecture bottles have a special

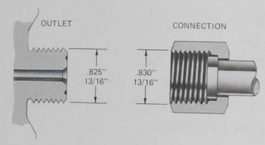


Fig. 1. CONNECTION 320 .825"-14 RH EXT. used with Flat Seat and Washer

5/16 inch-32 threads per inch female outlet and a 9/16 inch-18 threads per inch male dual valve outlet.

Safety Devices

Cylinders containing chlorotrifluoromethane have frangible discs as safety devices. Cylinders should, therefore, be stored away from sources of heat to avoid developing pressures capable of rupturing the disc.

Recommended Controls

To reduce the high cylinder pressure of chlorotrifluoromethane to a safe working value consistent with a system's design, the following types of controls are recommended.

Automatic Pressure Regulators

1. Single Stage Regulators

A single stage regulator will reduce cylinder pressure in one stage to a delivery pressure in a particular range, depending upon the design of the regulator and its spring load. A single stage regulator will show a variation in delivery pressure as cylinder pressure falls. The following Matheson single stage regulators are recommended for use with chlorotrifluoromethane:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
1P-320	28–240	0.28–2.4	4–35
1L-320	28–550	0.28–5.5	4–80
1H-320	69–1 240	0.69–12.4	10–180
2-320	340–4 480	3.4–44.8	50–650
3320 (with lecture bottles)	28–410	0.28–4.1	4–60
3321 (with lecture bottles)	28–410	0.28–4.1	4–60

Matheson

2. Two Stage Regulators

This type of regulator performs the same function as a single stage regulator. However, greater accuracy in control of delivery pressure is maintained and the delivery pressure does not vary as cylinder pressure falls. The following two stage regulators are recommended for use with chlorotrifluoromethane.

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
8L-320	14–104	0.14–1.04	2–15
8-320	28–340	0.28–3.4	4–50
8H-320	69–690	0.69–6.9	10–100
9-320	138–1720	1.38–17.2	20–250

To prevent suckback of foreign materials a check valve is recommended for use with the above regulators.

3. Low Pressure Regulators

Matheson Model 70 regulators are available for low pressure regulation. These regulators are constructed aluminum bodies, oversize Buna N rubber diaphragms, rubber seats, and brass needle valve outlets. The following low pressure regulators are available:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
70B	0.5–1.7	0.005–0.017	2–12 inches water column
70	3.4–34.5	0.034–0.345	0.5–5 psig
70A	34.5–69	0.345–0.69	5–10 psig

When the Model 70 regulator is used in series with the Model 1L-320 regulator (inlet pressure must not exceed 1724 kPa (250 psig)) a delivery pressure range of 3.4–34.5 kPa (0.5–5 psig) is obtainable.

Manual Controls

Matheson needle valve Model 50-320, a brass bar stock valve, is available for direct connection to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, 1/4" compression fitting or 1/4" NPT male or female pipe. It is used for intermittent flow control directly from the cylinder, but it requires constant attention by the user. It should not be used as a pressure control since dangerous pressures can develop if a line or the system itself becomes clogged. Needle valve Model 31B is recommended for use with lecture bottles.

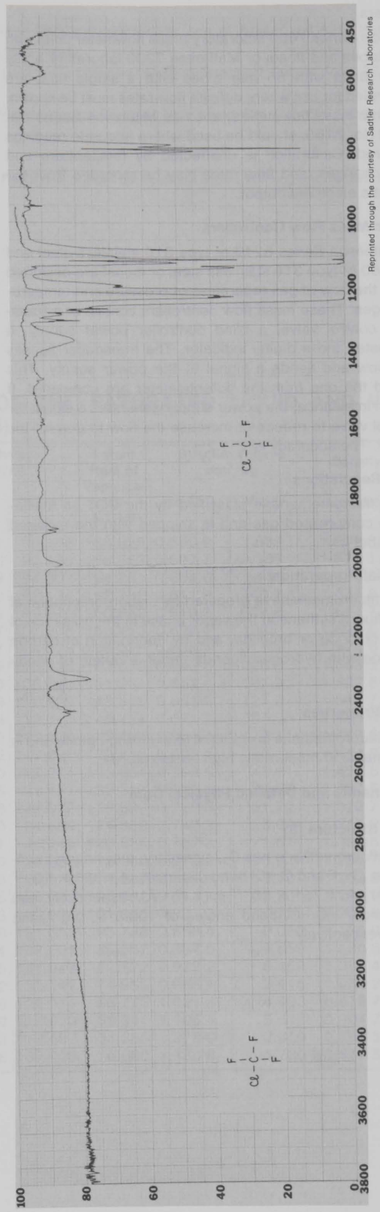


Fig. 2. Infrared spectrum of gaseous $CClF_3$ in the spectral region 3 800-450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure: curve A:2.67 kPa (20 mmHg); curve B (partial scan): 0.066 7 kPa (0.5 mmHg) (6).

Matheson

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and the one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Chlorotrifluoromethane is classified by the DOT as a nonflammable compressed gas and is shipped with the required "Green Label".

Commercial Preparation

Chlorotrifluoromethane is prepared by disporportionation of dichlorodifluoromethane in the vapor phase in the presence of aluminum chloride or bromide, and by fluorination of carbon tetrachloride with hydrogen fluoride under a variety of conditions.

Chemical Properties

Chlorotrifluoromethane is resistant to oxidizing agents and is thermally stable at moderately high temperatures.

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

Chlorotrifluoromethane has C_{3v} symmetry, a symmetry number of three, C—F and C—Cl bond distances of 1.328×10^{-10} m (1.328 Å) and 1.751×10^{-10} m (1.751 Å), respectively, and F—C—F and F—C—Cl bond angles of 108.5 ± 0.5 ° and 110.33 °, respectively.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous chlorotrifluoromethane.

Vapor Pressure (4)

Temperature, °C	Vapor Pressure kPa	bar	psia
−127.9	3.307	0.033	0.479 7
−100.5	32.221	0.322	4.674
−81.5	100.82	1.008	14.623
−57.9	305.99	3.06	44.38
−26.2	947.62	9.48	137.44
0.0	1 971.2	19.7	285.9
26.9	3 708.7	37.1	537.9

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔH_v, Temperature, °C	ΔH_v, kJ/kg
−125.0	167.455
−81.4	149.557
−60.0	137.891
−40.0	124.669
−20.0	108.635
0.0	88.248
20.0	56.635

Thermodynamic Data

See Tables 1 and 2 for the thermodynamic properties of the saturated liquid and vapor and the superheated vapor, respectively.

Thermodynamic Properties of Chlorotrifluoromethane as Ideal Gas @ 25 °C (3)

Heat Capacity, C_p°	66.885 J/(mol·°K)
	0.640 kJ/(kg·°K)
Entropy, S°	285.240 J/(mol·°K)
	2.731 kJ/(kg·°K)
Free Energy Function	−285.240 J/(mol·°K)
$(F_{298}^\circ - H_{298}^\circ)/T$	−2.731 kJ/(kg·°K)
Enthalpy, H°	13.782 kJ/mol
	0.132 kJ/kg
Enthalpy of Formation, ΔH_f°	−707.933 kJ/mol
	−6.777 kJ/kg
Free Energy of Formation, ΔF_f°	−667.390 kJ/mol
	−6.389 kJ/kg

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of chlorotrifluoromethane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 119–123, Matheson, Lyndhurst, New Jersey.

[3] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[4] L. F. Albright and J. J. Martin, *Ind. Eng. Chem.* 44, 188 (1952).

[5] *Thermodynamic Properties of Refrigerant* Freon-13, Tech. Bull. T-13A, *1968*, E. I. duPont de Nemours & Co., Wilmington, Delaware.

Table 1. THERMODYNAMIC PROPERTIES OF THE SATURATED LIQUID AND VAPOR (5)

Temperature °K	Temperature °F	Pressure kPa	Pressure bar	Entropy J/(kg·°K) Liquid	Entropy J/(kg·°K) Vapor	Enthalpy kJ/kg Liquid	Enthalpy kJ/kg Vapor	Latent Heat of Vaporization kJ/kg	Specific Volume dm³/kg Liquid	Specific Volume dm³/kg Vapor	Density kg/dm³ Liquid	Density kg/dm³ Vapor
144.26	−200	3.0	0.030	−417.60	752.70	−78.641	90.188	168.829	0.590 9	3 833	1.692 3	0.000 26
149.82	−190	5.1	0.051	−388.61	725.17	−74.378	92.485	166.863	0.597 7	2 305	1.673 1	0.000 43
155.37	−180	8.5	0.085	−360.28	700.74	−70.049	94.802	164.851	0.604 6	1 446	1.654 0	0.000 69
160.93	−170	13.5	0.135	−332.46	679.06	−65.652	97.134	162.786	0.611 9	940.7	1.634 3	0.001 06
166.48	−160	20.7	0.207	−305.14	659.77	−61.172	99.470	160.642	0.619 3	632.6	1.614 7	0.001 58
172.04	−150	30.7	0.307	−278.19	642.58	−56.607	101.806	158.413	0.627 1	438.0	1.594 6	0.002 28
177.59	−140	44.3	0.443	−251.58	627.22	−51.947	104.128	156.075	0.635 1	311.2	1.574 6	0.003 21
183.15	−130	62.5	0.625	−225.27	613.50	−47.189	106.429	153.618	0.643 6	226.3	1.553 8	0.004 42
188.71	−120	86.0	0.860	−199.24	601.12	−42.333	108.698	151.031	0.652 4	167.9	1.532 8	0.005 96
194.26	−110	116.0	1.16	−173.47	589.99	−37.379	110.929	148.308	0.661 5	127.0	1.511 7	0.007 87
199.82	−100	154.0	1.54	−147.95	579.90	−32.324	113.110	145.434	0.671 2	97.58	1.489 6	0.010 25
205.37	−90	200.0	2.00	−122.67	570.74	−27.170	115.234	142.404	0.681 4	76.11	1.467 6	0.013 14
210.93	−80	256.0	2.56	−97.61	562.37	−21.922	117.291	139.213	0.692 1	60.16	1.444 9	0.016 62
216.48	−70	324.0	3.24	−72.84	554.71	−16.580	119.274	135.854	0.703 5	48.11	1.421 5	0.020 79
222.04	−60	404.0	4.04	−48.33	547.60	−11.146	121.171	132.317	0.715 5	38.88	1.397 6	0.025 72
227.59	−50	498.0	4.98	−24.06	540.95	−5.618	122.972	128.590	0.728 5	31.72	1.372 7	0.031 53
233.15	−40	607.0	6.07	0.00	534.72	0.000	124.669	124.669	0.742 3	26.09	1.347 2	0.038 33
238.71	−30	733.0	7.33	23.81	528.77	5.711	126.245	120.534	0.757 3	21.61	1.320 5	0.046 28
244.26	−20	877.0	8.77	47.40	523.00	11.518	127.686	116.168	0.773 6	18.02	1.292 7	0.055 49
249.82	−10	1 040	10.40	70.84	517.31	17.429	128.976	111.547	0.791 4	15.10	1.263 6	0.066 22
255.37	0	1 224	12.24	94.10	511.66	23.456	130.088	106.632	0.811 1	12.70	1.232 9	0.078 74
260.93	10	1 431	14.31	117.28	505.80	29.613	130.994	101.381	0.833 2	10.72	1.200 2	0.093 28
266.48	20	1 661	16.62	140.50	499.70	35.929	131.652	95.723	0.858 4	9.062	1.165 0	0.110 35
272.04	30	1 918	19.18	163.85	493.04	42.444	132.001	89.557	0.887 5	7.659	1.126 8	0.130 56
277.59	40	2 203	22.03	187.61	485.60	49.225	131.947	82.722	0.922 2	6.459	1.084 4	0.154 82
283.15	50	2 518	25.18	212.05	476.81	56.382	131.347	74.965	0.965 1	5.415	1.036 2	0.184 67
288.71	60	2 866	28.66	237.99	465.80	64.138	129.911	65.773	1.021 8	4.483	0.978 7	0.233 06
294.26	70	3 251	32.51	267.06	450.37	73.029	126.970	53.941	1.105 4	3.612	0.904 7	0.276 86
299.82	80	3 683	36.83	307.02	421.37	85.412	119.697	34.285	1.278 0	2.659	0.782 5	0.376 08
302.00	83.93	3 870	38.70	364.22	364.22	102.908	102.908	0.000	1.730 8	1.730 8	0.577 8	0.577 78

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED $CC1F_3$ VAPOR (5)

H, ENTHALPY, kJ/kg; **S**, ENTROPY, J/(kg·°K); **V**, SPECIFIC VOLUME, dm^3/kg

Pressure kPa	Pressure psia		Temperature, °K 149.82	172.04	199.82	227.59	255.37	283.15	310.93	338.71	366.48	394.26	422.04	449.82	477.59
2.965	0.43	H	92.559	102.531	116.106	130.820	146.603	163.408	181.190						
		S	769.019	830.942	903.744	972.780	1 038.050	1 100.810	1 160.642						
		V	3 982	4 577	5 320	6 061	6 803	7 544	8 284						
20.684	3.00	H		102.066	115.757	130.564	146.417	163.269	181.051	199.739					
		S		675.298	748.936	817.972	883.661	946.421	1 006.252	1 063.991					
		V		654.7	764.0	872.5	980.6	1 088	1 196	1 303					
52.814	7.66	H			115.153	130.099	146.068	162.990	180.842	199.554					
		S			671.950	742.242	808.349	871.109	931.358	988.679					
		V			295.5	339.0	381.9	424.5	466.9	509.2					
100.112	14.52	H			114.200	129.425	145.533	162.572	180.516	199.275					
		S			617.977	689.105	756.049	819.227	879.477	937.216					
		V			153.0	176.6	199.8	222.6	245.2	267.7					
199.879	28.99	H				127.914	144.418	161.712	179.796	198.693	218.335				
		S				629.274	697.891	761.906	822.993	881.150	936.798				
		V				86.26	98.42	110.2	121.8	133.284	144.7				
497.801	72.20	H				122.963	140.838	158.992	177.634	196.927	216.871	237.442			
		S				540.991	615.048	682.410	745.170	804.583	861.067	915.459			
		V				31.72	37.44	42.70	47.71	52.57	57.33	62.03			
1 039.94	150.83	H					133.214	153.553	173.473	193.603	214.105	235.118			
		S					534.297	609.609	676.971	738.894	797.052	852.281			
		V					15.81	18.95	21.72	24.30	26.76	29.15			
2 056.98	298.34	H						140.420	164.547	186.816	208.665	230.608	252.783		
		S						519.653	600.822	669.440	731.363	789.102	843.494		
		V						7.810	9.795	11.41	12.86	14.22	15.51		
3 053.34	442.85	H							153.390	179.308	202.947	225.982	248.925	271.983	
		S							540.991	620.906	688.268	748.518	805.002	857.720	
		V							5.631	7.048	8.197	9.227	10.18	11.09	
4 163.67	603.89	H							132.261	169.405	195.997	220.566	244.485	268.241	
		S							458.148	573.208	648.520	713.372	771.948	826.340	
		V							2.897	4.576	5.606	6.468	7.242	7.960	
5 143.21	745.96	H								158.690	189.303	215.569	240.487	264.917	289.207
		S								530.531	617.558	686.594	747.681	803.746	856.046
		V								3.221	4.239	5.019	5.700	6.324	6.911
6 137.92	890.23	H								145.719	181.957	210.316	236.349	261.500	286.325
		S								484.089	587.015	661.909	725.506	783.245	836.800
		V								2.285	3.296	4.027	4.645	5.200	5.718
6 388.68	926.60	H								142.465	180.051	208.968	235.303	260.640	285.581
		S								472.792	579.902	656.051	720.485	778.642	832.616
		V								2.110	3.103	3.827	4.432	4.976	5.475

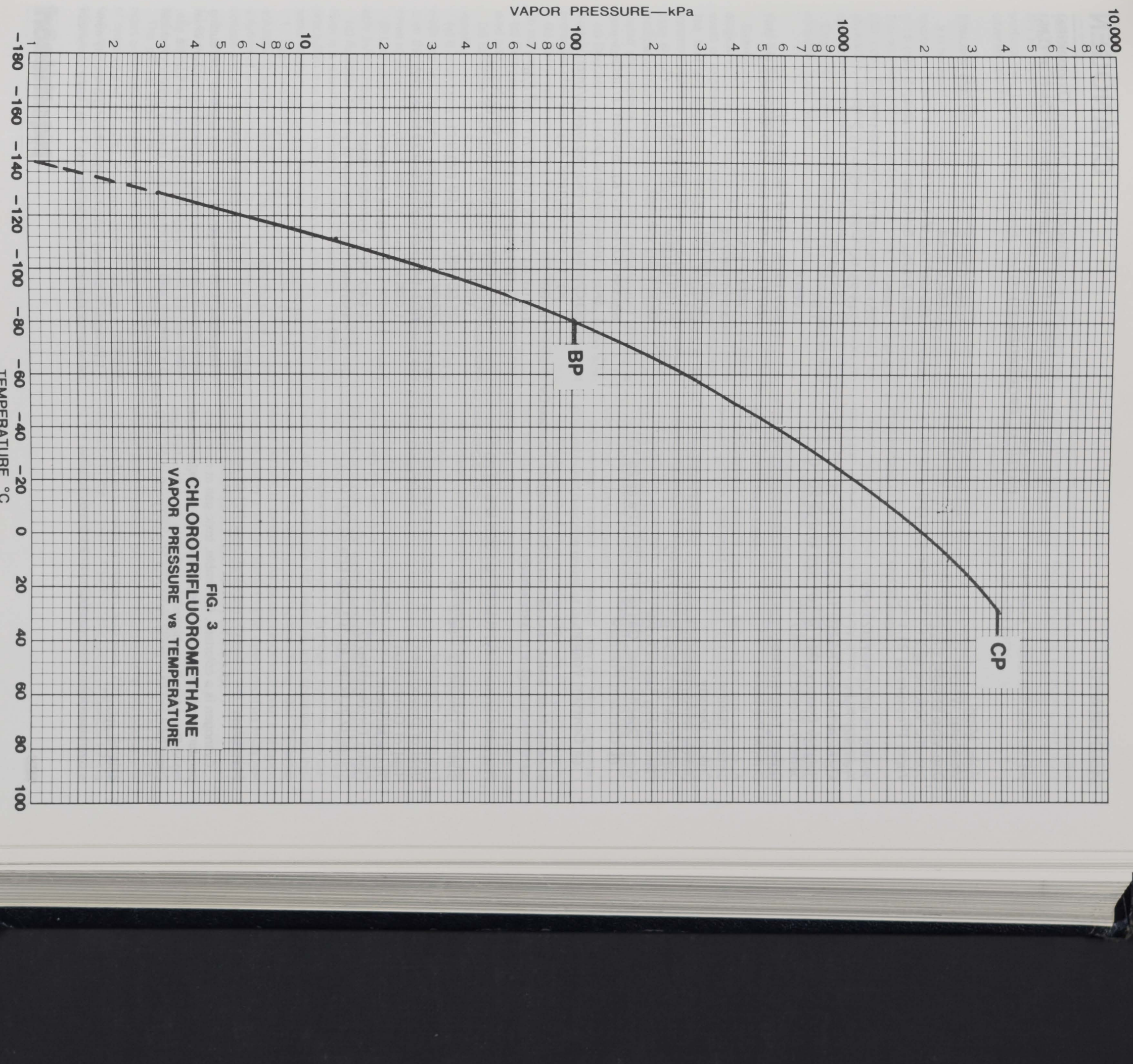


FIG. 3
CHLOROTRIFLUOROMETHANE
VAPOR PRESSURE vs TEMPERATURE

Matheson

CYANOGEN

(Synonyms: Dicyan; Oxalonitrile)
(Formula: N≡C—C≡N or C_2N_2)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.052 035 kg
One Mole of C_2N_2	0.052 035 kg
Specific Volume @ 21.1 °C, 101.325 kPa	462 dm^3/kg; 7.4 ft^3/lb
Vapor Pressure @ 21.1 °C	515.7 kPa; 5.16 bar; 74.8 psia; 5.09 atm
Boiling Point @ 101.325 kPa	251.98 °K; −21.17 °C; −6.1 °F
Freezing Point	245.25 °K; −27.9 °C; −18.2 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	2.189 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C	1.817
Density, Liquid @ −40 °C	0.989 6
Critical Temperature	400.15 °K; 127.0 °C; 260.6 °F
Critical Pressure	5978 kPa; 59.78 bar; 59.0 atm; 867.1 psia
Critical Volume	3.844 dm^3/kg
Critical Density	0.260 kg/dm^3
Critical Compressibility Factor	0.275
Latent Heat of Fusion @ −27.9 °C	8.109 kJ/mol; 155.83 kJ/kg
Flammability Limits In Air	6–32% (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	58.338 kJ/(kmol·°K); 58.338 J/(mol·°K); 13.943 cal/(mol·°C)
@ Constant Volume	50.024 kJ/(kmol·°K); 50.024 J/(mol·°K); 11.956 cal/(mol·°C)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.166
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.010 70 mPa·s; 0.010 70 $mN·s/m^2$; 0.010 70 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.014 66W/(m·°K); 35.04 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −56.2 °C	21.98 mN/m; 21.98 dyn/cm
Trouton's Constant	22.94
Heat of Dissociation	502–544 kJ/mol; 120–130 kcal/mol
Heat of Combustion	1 096 kJ/mol; 261.94 kcal/mol
Dipole Moment	1.27 ×10^{-30} C·m; 0.38 D
Flame Temperature/O_2	4 640 °K; 4 367 °C; 7 893 °F
Solubility In Water @ 101.325 kPa @ 20 °C	450 cm^3 C_2N_2/100 cm^3 H_2O

Description

Cyanogen is a colorless, flammable, toxic gas at room temperature and atmospheric pressure with a characteristic almond-like odor. It is shipped in cylinders as a liquefied gas under its own vapor pressure of 414 kPa (60 psig) at 21.1 °C.

Specifications

Cyanogen has a minimum purity of 98.5% by volume.

Uses

Cyanogen is of interest as a gas for welding and cutting heat-resistant metals, as a rocket and missile propellant when mixed with an oxidizing agent such as ozone or fluorine gas, as a fumigant, and as an intermediate in many organic chemical syntheses.

Toxicity

Cyanogen is a highly poisonous gas, having a toxicity comparable to that of hydrogen cyanide. The 1979 American Conference of Governmental Industrial Hygienists (ACGIH) has established a Threshold Limit Value (TLV) of 10 ppm (20 mg/m^3) for cyanogen (concentration in air to which nearly all workers may be repeatedly exposed, day after day, without adverse effects).

Effects in Man (2)

It is believed that cyanogen is converted in the body partly to hydrocyanic acid and partly to cyanic acid (HOCN). Exposure to 16 ppm for 6–8 minutes produced eye and nasal irritation. The odor was not detected at these concentrations nor at 50–250 ppm. Effects observed during exposures included asphyxiation, lacrimation, upper respiratory tract irritation, incoordination, tremors and prostration.

Cyanogen is not readily detectable by odor except in high concentrations, when it becomes pungent.

First Aid Suggestions (3)

Cyanogen is closely allied to hydrogen cyanide in its physiological action so that the first aid procedures developed in the event of exposure to hydrogen cyanide are being presented. The first aid suggestions which follow are believed to be common practice in industry. Their adoption in any specific case should be subject to prior endorsement by a competent medical advisor. Speed in removing the victim from the contaminated atmosphere and in removing contaminated clothing is essential.

(a) Rescuers entering a contaminated area *must* be adequately protected with self-contained breathing apparatus and protective clothing.

(b) Carry victim to a room free of gas and have him lie down. Do not permit the victim to exert himself.

(c) Remove contaminated clothing but keep the patient covered and comfortably warm.

(d) Summon a physician for anyone exposed to cyanogen vapors.

(e) If cyanogen is inhaled, break an amyl nitrite pearl in a cloth and hold it lightly under the nose of the victim (but away from the person giving first aid) for 15 seconds. Repeat five times at about 15 second intervals.

(f) Use artificial respiration if breathing has stopped, preferably by the Holger-Nielsen method.

(g) Antidote. Note to Physicians: The Nitrite-Thiosulfate regimen is a specific antidote for cyanide poisoning. The following procedure has been found to be very effective. It should be administered *only under the direction of a physician*.

1. Load two syringes without delay, one with 10 cc of a 3% solution of sodium nitrite and the other with 50 cc of a 25% solution of sodium thiosulfate. Only a specially prepared intravenous solution in ampules should be used.
2. Stop administration of amyl nitrite and inject intravenously 10 cc of 3% sodium nitrite at the rate of 2.5–5 cc per minute.
3. Inject by the same needle and vein, or by a large needle and a new vein, 50 cc of 25% sodium thiosulfate solution.

The patient should be watched for at least 24–48 hours. If signs of poisoning reappear (giddiness, headache, fatigue, loss of appetite and nausea), injection of both sodium nitrite and sodium thiosulfate should be repeated, but each in one-half the original dose. Even if the patient looks perfectly well, the medication may be given for prophylactic purposes, two hours after the first injections.

Users of cyanogen should have readily available for the doctor a kit containing the following items:

12 pearls of amyl nitrite
1 sterile syringe, 10 cc
1 sterile syringe, 50 cc
2 ampules of sodium nitrite (10 cc, 3% solution)
2 ampules of sodium thiosulfate (50 cc, 25% solution)

Precautions in Handling and Storage

(a) In view of the lethal nature of cyanogen, the handling of cyanogen should be undertaken only after the properties of cyanogen, its toxicity and the proper safety and emergency measures have been thoroughly reviewed.

(b) Self-contained breathing apparatus should be instantly available for use in emergencies.

(c) Cyanogen should be handled only in a well-ventilated area, preferably a hood.

(d) Cyanogen should never be handled by one person. A second person, stationed at a safe distance, should also be present.

(e) Workers handling cyanogen should wear rubber gloves, rubber protective clothing and rubber-soled shoes at all times.

(f) Adequate emergency showers and wash-up facilities should be available for use when working with cyanogen.

(g) Open flames or electrical equipment which is not explosion-proof must be avoided.

(h) Cyanogen should be handled only in small amounts, preferably not over one pound at one time.

(i) Waste disposal of cyanogen, and materials containing it, depends to a great extent on local conditions. All local, state and federal regulations regarding health and pollution must be followed.

(j) Store full and empty cylinders separately and away from oxidizing gases.

In addition, the general rules listed in appendix I should be observed.

Leak Detection

Equipment to contain cyanogen should be pretested for leaks with dry nitrogen. The presence of cyanogen in air may be detected with moist methyl orange-mercuric chloride test papers (color changes from orange to pink to red at relatively low concentrations of cyanogen). Hydrogen cyanide gas detectors are also available for sensitive and accurate on-the-spot testing. The Matheson-Kitagawa Toxic Gas Detector Model 8014K is available for accurate detection of hydrogen cyanide. Using a Model 8014-112SB direct-reading HCN detector tube (2-100 ppm) hydrogen cyanide can be detected quickly. Readings are read directly off the tube.

Disposal of Leaking Cylinders

Leaks in cylinders containing cyanogen which cannot be corrected by normal procedures can be disposed of as follows. Put on self-contained breathing equipment. If the cylinder is not already in a hood, transport it to one. Attach a suitable regulator to the cylinder. Attach a long piece of flexible tubing to the outlet of the regulator. Extend the free tube end into a

dilute solution containing excess sodium hydroxide and excess sodium hypochlorite contained in an iron or steel drum or other suitable vessel. The rate of introduction of cyanogen into the solution is adjusted to a slow to moderate rate. When all of the gas has been introduced, remove the flexible tubing, close the opening of the drum, and let stand 24 hours. The solution is now ready for disposal, the cyanogen having been oxidized to sodium cyanate.

Materials of Construction

Glass-lined equipment is satisfactory for conveying or processing cyanogen. Stainless steel, monel and inconel are also satisfactory up to at least 65 °C.

Cylinder and Valve Description

Cyanogen is shipped in DOT approved steel, cylinders. Cylinders are equipped with Compressed Gas Association (CGA) No. 660 valve outlet connection, the approved alternate. The valve outlet has a thread size of 1.030" diameter with right-hand external threads, with a connector having a flat seat and washer (see Figure 1 for an illustration of this valve outlet and its mating connection).

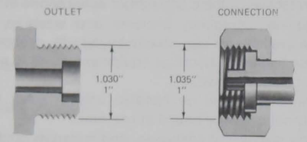


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders of cyanogen are not equipped with safety devices. They should, therefore, be stored away from sources of heat to prevent dangerous hydrostatic pressure from developing within the cylinder.

Recommended Controls

Automatic Pressure Regulators

Regulator Model 19C-660, a diffusion-resistant metal diaphragm regulator, is recommended for use with cyanogen. It is a brass construction with a German silver diaphragm plus a packless control valve. It has a delivery pressure range of 28–340 kPa (4–50 psig).

Manual Controls

Matheson stainless steel needle valve Model 61A-660 is recommended for use with cyanogen. It should be used only when intermittent flows are required.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%

Shipping Regulations

Cyanogen is classified by the DOT as a "Class A" poison and Flammable gas and is shipped under the required "Poison Gas Label" and "Red Gas Label".

Chemical Preparation

On a laboratory scale, the addition of an aqueous solution of potassium cyanide to a concentrated solution of copper sulfate at 60–100 °C had been widely used. Other methods (4) involve air oxidation of hydrogen cyanide over a silver catalyst at 300–600 °C, passage of hydrogen cyanide into a mixture of copper(II) oxide at ambient temperatures, by the reaction of hydrogen cyanide and chloride over a surface-active material (such as activated carbon) at temperatures over 700 °C, by dehydration of ammonium oxalate, oxamide, or glyoxime, or by electrolysis of aqueous hydrogen cyanide.

Chemical Properties

Water dissolves four volumes of cyanogen. The solution, on standing, gradually decomposes into ammonium oxalate and formate, hydrogen cyanide and urea, while at the same time brown amorphous azulmic acid separates. Cyanogen is hydrolyzed in concentrated hydrochloric acid or concentrated acetic acid principally to oxamide; in the latter, hydrolysis urea is also formed. Cyanogen brought into contact with an aqueous solution of a carboxylic acid or a phosphorous-containing acid at 50 to 90 °C forms cyanoformamide. Oxamide and ammonium oxalate are obtained in low yields when cyanogen is passed into aqueous solutions of sulfuric or phosphoric acid which contain zinc, cadmium, magnesium and mercury compounds. Almost complete conversion to oxamide is realized when cyanogen is sparged at 40 °C into a 25% sulfuric acid solution containing mercury(II) oxide. The products obtained from the reaction of cyanogen with reducing acids depend on the acid and the conditions employed. In the absence of air, cyanogen and sulfurous acid react at room temperature to give hydrogen cyanide and sulfuric acid. In the presence of refluxing hydriodic acid, cyanogen is converted into glycine, ammonium iodide and iodine. Cyanogen is hydrolyzed in dilute potassium and sodium hydroxide solutions to the corresponding cyanide and cyanate. Cyanogen reacts with potassium amide in liquid ammonia to form potassium cyanide and potassium cyanamide. Sodium amide forms sodium cyanamide and ammonium cyanide.

Cyanogen and liquid hydrogen sulfide react in equimolar quantities to form thiocyanoformamide, and in a 2:1 molar ratio to form dithiooxamide. The latter is also formed when cyanogen is sparged into an aqueous solution of sodium hydrogen sulfide.

Cyanogen polymerizes to paracyanogen when heated to 300 °C or by exposure to ultraviolet light. Paracyanogen is reconverted to cyanogen at about 800 °C.

A comprehensive study was made by Welcher, **et al.** (5), on the stability of pure cyanogen to heat, pressure, chemical additives and severe mechanical shock. Pure cyanogen remained unchanged after 18–23 days at 65 °C and contained only small quantities of solid decomposition products after storage for 100 days under similar conditions.

Cyanogen reacts with a variety of organic compounds such as: aliphatic, aromatic and heterocyclic amines and diamines, hydrazine and hydroxlamine and derivatives, hydrazoic acid and diazoalkanes, guanidines and thioureas, Grignard and related reagents, phenols, thiols and thiophenols, alcohols and glycols, and compounds containing active hydrogen or carbon aldehydes. The products of the above reactions are given in the review article cited, as well as original references.

Thermodynamic and Detailed Physical Data

Molecular Structure

The cyanogen molecule is symmetrical and linear, having a symmetry number of two and belonging to point group D∞h. The C≡N bond distances are 1.15×10^{-10} m (1.15 Å) and the C—C bond distance is 1.380×10^{-10} m (1.380 Å).

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous cyanogen.

Vapor Pressure (6)

For vapor pressure data above and below 101.325 kPa, see the following table.

Temperature, °C	Vapor Pressure kPa	bar	mmHg = torr
−95.8	0.13	0.001 3	1
−83.2	0.67	0.006 7	5
−76.8	1.32	0.013 2	10
−70.1	2.63	0.026 3	20
−62.7	5.37	0.053 7	40
−57.9	8.00	0.080 0	60
−51.8	13.2	0.132	100
−42.6	26.3	0.263	200
−33.0	53.7	0.537	400
−21.0	101.325	1.013 25	760
−4.4	202.6	2.026	1 520
21.4	506.6	5.066	3 800
44.6	1 013.2	10.132	7 600
72.6	2 026.5	20.265	15 200
91.6	3 039.8	30.398	22 800
106.5	4 053.0	40.530	30.400

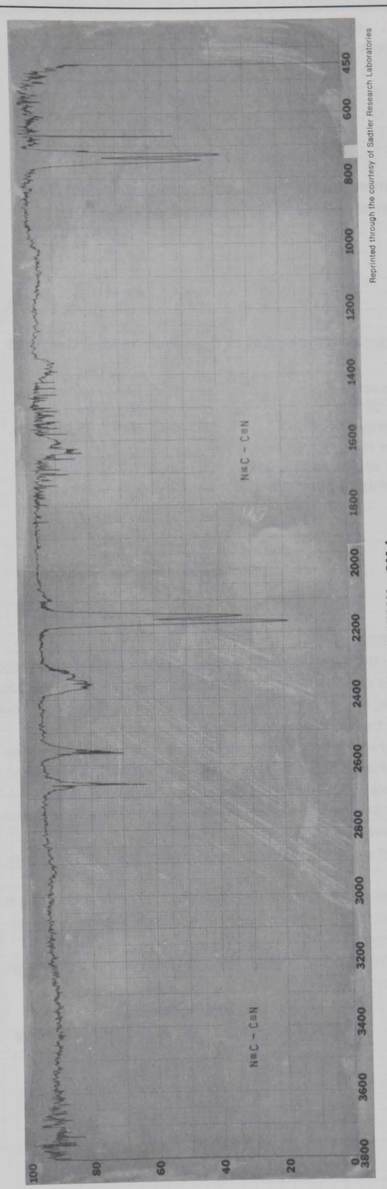


Fig. 2. Infrared spectrum of gaseous cyanogen in the spectral range 3 800–450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure 8.0 kPa (60 mmHg) (10).

CYANOGEN

Temperature, °C	Vapor Pressure kPa	bar	mmHg = torr
118.2	5 066.2	50.662	38.000
127.0 (C.T.)	5 978.2	59.782 (C.P.)	44 840

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv (calculated) (7)

Temperature, °C	ΔHv, kJ/mol
−28.0	24.899
−21.2	24.175
0.0	22.476
20.0	21.518
40.0	19.100

Thermodynamic Properties of Cyanogen As Ideal Gas @ 25 °C (8)

Heat Capacity, C_p°	56.748 J/(mol·°K)
Entropy, S°	241.463 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/T$	−241.463 J/(mol·°K)
Enthalpy of Formation, ΔH_f°	309.072 kJ/mol
Free Energy of Formation, ΔF_f°	297.554 kJ/mol

Compressibility Data (9)

See Table 1 for data.

Table 1. COMPRESSIBILITY DATA FOR CYANOGEN (11)

Temperature, °C	Pressure kPa 137.9	275.8	413.7	689.5
−6.7	0.998 1			
−1.1	0.998 2			
4.4	0.998 3	0.996 6		
10.0	0.998 4	0.996 7		
15.6	0.998 5	0.996 9	0.995 3	
21.1	0.998 6	0.997 1	0.995 5	
26.7	0.998 6	0.997 2	0.995 7	
32.2	0.998 7	0.997 3	0.995 9	0.993 0
37.8	0.998 7	0.997 5	0.996 1	0.993 4
43.3	0.998 8	0.997 6	0.996 3	0.993 7
48.9	0.985 1	0.969 3	0.952 0	0.910 9

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of cyanogen, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment* 2nd edition, *1977*, pp. 32–38, Matheson, Lyndhurst, New Jersey.

[3] W. Braker and A. L. Mossman, *Matheson Gas Data Book*, 5th edition, *1971*, pp. 155–156, Matheson, East Rutherford, New Jersey.

[4] T. K. Brotherton and J. W. Lynn, *Chem. Rev.* 59, 844–850 (1959).

[5] R. P. Welcher, *et al.*, *Ind. Eng. Chem.* 49, 1755 (1957).

[6] *Chemical Engineers' Handbook*, 4th edition, R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, editors, *1963*, pp. 3–50, 3–59, McGraw-Hill Book Co., Inc., New York, New York.

[7] R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids*, 2nd edition, *1966*, pp. 148–149, McGraw-Hill Book Co., Inc., New York, New York.

[8] JANAF Thermochemical Tables, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[9] See reference 3, p. 159.

[10] The Sadtler Standard Spectra, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[11] See reference 3, p. 159.

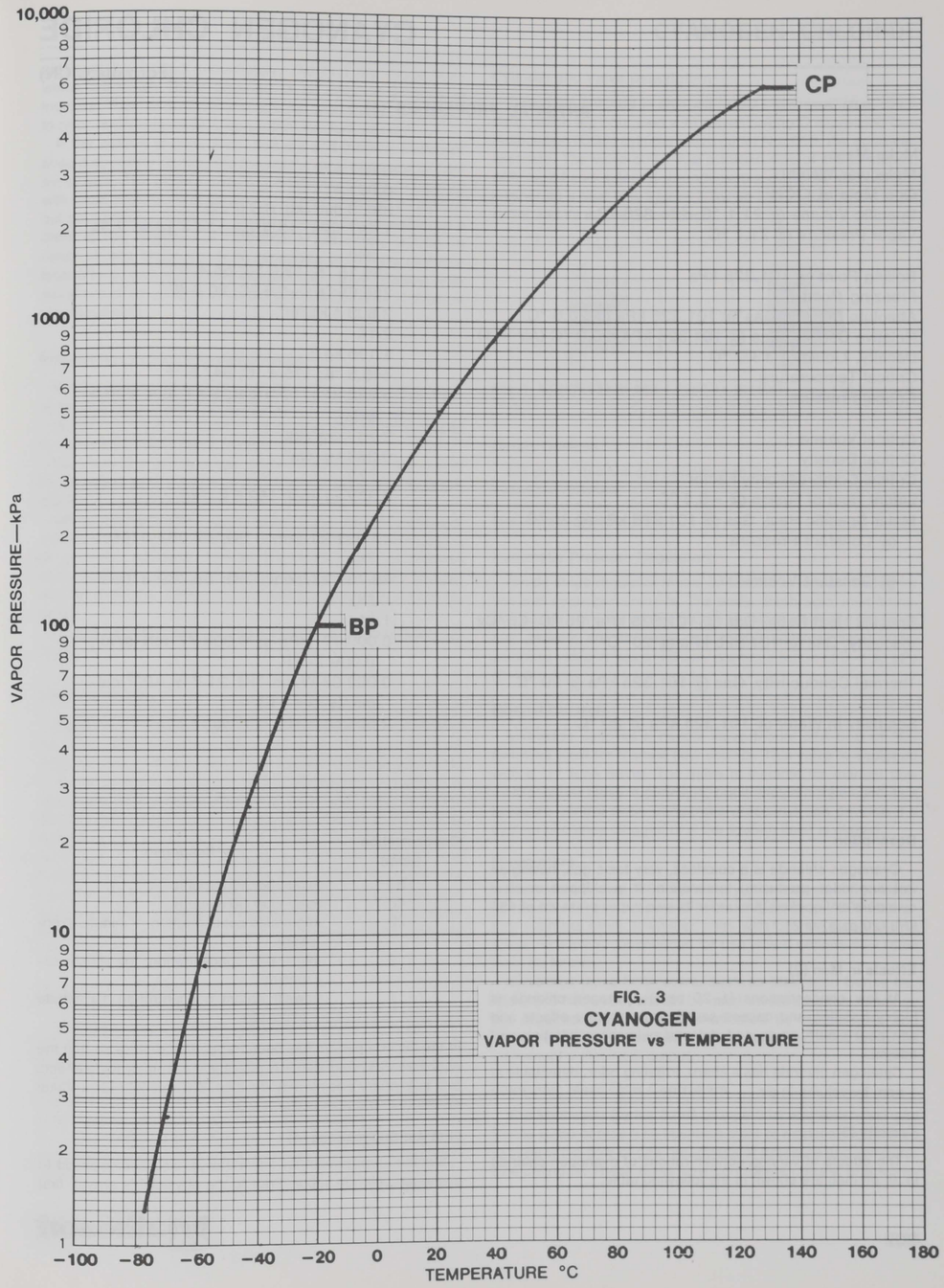


FIG. 3
CYANOGEN
VAPOR PRESSURE vs TEMPERATURE

CYANOGEN CHLORIDE

(Formula:CICN)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.061 471
One Mole of CICN	0.061 471
Specific Volume @ 21.1 °C, 101.325 kPa	393.3 dm^3/kg; 6.3 ft^3/lb
Vapor Pressure @ 21.1 °C	1 987 kPa; 19.9 bar; 34.4 psia; 2.34 atm
Boiling Point @ 101.325 kPa	286.15 °K; 13.0 °C; 55.4 °F
Freezing Point	266.65 °K; −6.5 °C; 20.3 °F
Absolute Density, Gas @ 101.325 kPa @ 20.0 °C	2.603 4 kg/m^3
Relative Density, Gas @ 101.325 kPa, 20.0 °C (Air = 1)	2.16
Density, Liquid @ 13.0 °C	1.196 kg/l
Critical Temperature	448.5 °K; 175.4 °C; 347.6 °F
Critical Pressure	5 988 kPa; 59.9 bar; 59.1 atm; 868.5 psia
Critical Volume	2.757 dm^3/kg
Critical Density	0.363 kg/dm^3
Critical Compressibility Factor	0.273
Latent Heat of Fusion @ −6.5 °C	9.372 kJ/mol; 152.5 kJ/kg
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	47.083 kJ/(kmol·°K); 47.083 J/(mol·°K)
@ Constant Volume	38.769 kJ/(kmol·°K); 38.769 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa, 25 °C, Cp/Cv	1.214
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.009 77 mPa·s; 0.009 77 $mN·s/m^2$; 0.009 77 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 20 °C	0.009 08 W/(m·°K); 21.7 × 10^{-6} cal·cm/(s·cm^2·°C)
Solubility In Water @ 101.325 kPa @ 20 °C	2 500 cm^3/100 cm^3 water

Description

Cyanogen chloride is a colorless, very toxic gas, having an irritating odor producing lacrimation. It is shipped in steel cylinders as liquefied gas under its own vapor pressure of 136 kPa (20 psig) at 21.1 °C.

Effects in Man (2)

At low concentrations (1–20 ppm) cyanogen chloride is highly irritating and causes severe lachrymatory effects and can cause both acute and delayed pulmonary irritation and edema.

Cyanogen chloride has a sharp, irritating odor, detectable at 1 ppm by volume in air.

Toxicity (3)

The effects of varying concentrations of cyanogen chloride in air on man are shown in the following table.

Concentration (ppm)	Response
159	Fatal after 10 minutes
48	Fatal after 30 minutes
20	Intolerable concentration, 1 minute exposure
2	Intolerable concentration, 10 minute exposure
1	Lowest irritant concentration 10 minute exposure

In the event a person has been trapped in an area so that the exposure was prolonged, it is possible that both cyanide effects and pulmonary edema may develop. A Threshold Limit Value of less than 0.5 ppm is suggested.

First Aid Suggestions (4)

Summon a physician for anyone who has been exposed to cyanogen chloride vapor. Prior to the physician's arrival, first aid must be started immediately. The first aid suggestions which follow are those believed to be common practice in industry. Their adoption in any specific case should be subject to prior endorsement by a competent medical advisor.

If the patient is conscious, first aid and medical treatment should generally be directed toward the relief of any pulmonary symptoms. The patient should immediately be put at bedrest with head slightly elevated and a medical examination carried out as quickly as possible. Oxygen should be administered if there is any dyspnea or evidence of pulmonary edema. In cases of long exposures (with symptoms of both the cyanide-type effects and pulmonary edema), combined therapy, with oxygen plus amyl nitrite inhalations and artificial respiration, is recommended.

Precautions in Handling and Storage

(a) Cyanogen chloride should be handled only in a well-ventilated area, preferably a hood with forced ventilation.

(b) Self-contained breathing apparatus should be available in convenient locations in emergencies.

(c) Areas in which cyanogen chloride is being handled should be provided with enough exits to permit personnel to leave quickly in case of trouble.

(d) An acid-gas and organic vapor mask, NIOSH-approved, are recommended for respiratory protection in concentrations of up to 2% cyanogen chloride. Where the cyanogen chloride concentration may at any time exceed 2% or where oxygen may be deficient, self-contained breathing apparatus must be used.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Equipment to contain cyanogen chloride should be pretested for leaks with dry compressed air or an inert gas such as nitrogen. The pungent odor of cyanogen chloride is detectable in concentrations as low as 1 ppm. A colorimetric method is described for the determination of cyanogen chloride in the atmosphere. Leaks at the cylinder valve may be eliminated by tightening the stem, packing nut or cap. If a cylinder leak is such that it cannot be stopped by ordinary methods, the supplier should be called immediately; in the meantime, the cylinder should be removed from the storage or use area and exhausted into a caustic absorption system, or the cylinder should be moved outdoors to a location where it can gradually lose its contents without damage or hazard.

Materials of Construction

Cyanogen chloride, when used in anhydrous equipment with anhydrous reagents, is not corrosive to ordinary metals under normal conditions of use (room temperature and atmospheric pressure). In the presence of moisture, however, corrosive conditions will develop rapidly, in which case monel, tantalum, or glass or glass-lined equipment may be used.

Piping and vessels to contain cyanogen chloride should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

Cyanogen chloride is shipped in DOT approved steel cylinders, which are equipped with valves having Compressed Gas Association (CGA) cylinder valve outlet No. 660, the approved alternate. The valve outlet has a thread size of 1.030 inches, with right-hand external threads with a flat seat and using a washer as a seal (see Figure 1 for an illustration of this valve outlet and its mating connection).

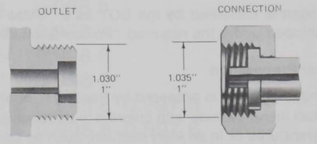


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

Safety Devices

No safety devices are permitted to be used on cylinders of cyanogen chloride.

Recommended Controls

Automatic Pressure Regulators

Single stage regulator Model 3455-660 is recommended for use with cyanogen chloride. The body, diaphragm, inlet fitting, and gauge are constructed of 316 stainless steel and the seats and gaskets are Teflon. It has a 303 stainless steel outlet packless valve. It has a delivery pressure range of 0–138 kPa (0–20 psig).

Manual Controls

Matheson supplies a needle valve Model 61A-660 of 303 stainless steel for manual flow control. This valve is equipped with a ¼" tube fitting. The valve is suitable for manual flow control under close supervision, but it should not be used as a pressure control since dangerous pressures can develop if a system becomes clogged or if the system itself is closed.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a trans-

ducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Cyanogen is classified by the DOT as a "Class A" poison and is shipped under the required "Poison Gas Label".

Chemical Preparation

Cyanogen chloride is prepared by treating hydrocyanic acid or an alkali metal cyanide with chlorine in aqueous solutions at low temperatures or in an inert medium, such as carbon tetrachloride or ethylene chloride, or by chlorinating an aqueous suspension of potassium zinc cyanide.

Chemical Properties

In the presence of alkali, cyanogen chloride is hydrolyzed to the metal chloride and metal cyanate. Cyanogen chloride reacts with olefins giving cyanoolefins, cyanoalkanes, ω-chloro-cyanoalkanes, and other products, depending on the catalyst and reaction conditions. Polymerization of cyanogen chloride to cyanuric chloride is favored by the presence of hydrogen chloride and thus is favored by the presence of moisture because of partial hydrolysis. Chlorine also favors polymerization to cyanuric chloride. Cyanogen chloride reacts quantitatively on heating with aqueous solutions of hydrogen iodide, sulfur dioxide, and hydrogen sulfide giving hydrogen cyanide and hydrogen chloride as well as iodine, sulfuric acid, and sulfur, respectively. In the presence of alkaline reducing agents, such as sodium sulfite and sodium hydroxide, cyanogen chloride gives sodium cyanide, sodium chloride, and sodium sulfate. Cyanogen chloride reacts with ammonia in ether or in aqueous solution giving cyanamide and ammonium chloride. Cyanogen chloride reacts with hydrazine (1:2 molar ratio) in aqueous solution, giving chiefly sym-diaminoguanidine hydrochloride. Aqueous solutions of cyanogen chloride are not precipitated by silver nitrate. Alcoholic solutions of cyanogen chloride decompose in a short time giving diethyl carbonate, ethyl carbamate, a little ethyl chloride and ammonium chloride. Cyanogen chloride does not react with alcohol-free sodium ethoxide; however, in the presence of absolute alcohol, there is formed at −10 °C diethyl iminocarbonate, while at room temperature this same compound is formed along with triethyl cyanurate. Cyanogen chloride reacts with methylamine to give methylcyanamide and sym-dimethylguanidine. Cyanogen chloride also reacts with aniline, phenylhydrazine, diazoethane and diazomethane.

Thermodynamic and Detailed Physical Data

Molecular Structure

The cyanogen chloride molecule is linear, with $C_{\infty v}$ symmetry, having a symmetry number of one. The Cl—C and C≡N bond distances are 1.631×10^{-10} m (1.631 Å) and 1.162×10^{-10} m (1.162 Å), respectively. The Cl—C≡N bond angle is 180°.

Vapor Pressure

The vapor pressure of liquid cyanogen chloride from −5.0 °C to 40.0 °C is represented by the following equation (5):

$$\log_{10} p = 7.840\text{-}1\ 418.953T$$

in which p = mmHg and T = °K.

Some calculated vapor pressures are compared with reported values (5) in the following table.

Vapor Pressure

Temperature, °C	Reported Values (5)			Calculated Values		
	kPa	mbar	mmHg	kPa	mbar	mmHg
−76.7	0.133	1.333	1			
−61.4	0.667	6.666	5			
−53.8	1.333	13.33	10			
−46.1	2.666	26.66	20			
−37.5	5.333	53.33	40			
−32.1	7.999	79.99	60			
−24.9	13.33	133.3	100			
−14.1	26.6	266.6	200			
−2.3	53.3	533.3	400	53.20	532.0	399
0.0	59.33	593.3	445 (6)	59.06	590.6	44.3
2.0	64.53	645.3	484 (6)	64.26	642.6	482
4.0	70.26	702.6	527 (6)	69.99	699.9	525
6.0	76.39	763.9	573 (6)	76.13	761.3	571
8.0	82.79	827.9	621 (6)	82.79	827.9	621
10.0	89.86	898.6	674 (6)	89.86	898.6	674
15.40	101.325	1 013.25	760	101.86	1 018.6	764
20.0				133.19	1 331.9	999
40.0				271.58	2 715.8	2 037

Latent Heat of Vaporization, ΔHv

Temperature, °C	ΔHv, kJ/mol
−8.0	27.677
0.0	27.150
10.0	26.623
13.0	26.359
20.0	25.832
30.0	25.041

Thermodynamic Properties of Cyanogen Chloride As Ideal Gas @ 25 °C (7)

Heat Capacity, C_p°	45.271 J/(mol·°K)
Entropy, S°	236.224 J/(mol·°K)
Free Energy Function, $(F^\circ_{298}\text{-}H^\circ_{298})/T$	−236.224 J/(mol·°K)
Enthalpy, H°	10.686 kJ/mol
Enthalpy of Formation ΔH°_f	137.946 kJ/mol
Free Energy of Formation, ΔF°_f	130.997 kJ/mol

Compressibility Data

See Table 1 for compressibility data for cyanogen chloride.

Table 1. COMPRESSIBILITY DATA FOR CYANOGEN CHLORIDE

Temperature, °C	Pressure, kPa 137.9 (20 psia)	275.8 (40 psia)	413.7 (60 psia)	551.6 (80 psia)
−6.7	0.983 8			
−1.1	0.984 8			
4.4	0.998 5			
10.0	0.998 6			
15.6	0.998 6			
21.1	0.998 7			
26.7	0.998 8	0.997 5		
32.2	0.998 8	0.997 6		
37.8	0.998 9	0.997 7	0.996 5	
43.3	0.998 9	0.997 8	0.996 7	
48.9	0.999 0	0.997 9	0.996 8	0.994 6

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of cyanogen chloride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 32–38, Matheson, Lyndhurst, New Jersey.

[3] F. A. Patty, *Industrial Hygiene and Toxicology, 1962*, Volume II, pp. 2005–2007, Interscience Publishers, New York, New York.

[4] W. Braker and A. L. Mossman, *Matheson Gas Data Book, 1971*, 5th edition, p. 161, Matheson, East Rutherford, New Jersey.

[5] *Chemical Engineers' Handbook*, R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, editors, *1963*, 4th edition, p. 3–107, McGraw-Hill Book Co., Inc., New York, New York.

[6] A. Klemenc and G. Wagner, *Z. Anorg. Chem. 235*, 427 (1938).

[7] JANAF Thermochemical Tables, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

CYCLOBUTANE

(Synonym: Tetramethylene)
(Formula: C_4H_8)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.056 108 kg
One Mole of C_4H_8	0.056 108 kg
Specific Volume @ 21.1 °C, 101.325 kPa	430.7 dm^3/kg; 6.9 ft^3/lb
Vapor Pressure @ 21.1 °C	158.6 kPa; 1.59 bar; 23.0 psia; 1.56 atm
Boiling Point @ 101.325 kPa	285.66 °K; 12.5 °C; 54.5 °F
Triple Point	182.42 °K; −90.7 °C; −131.3 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	2.405 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	1.996
Density, Liquid @ Saturation Pressure @ 25 °C	0.689 kg/dm^3
Critical Temperature	457.99 °K; 184.8 °C; 364.7 °F
Critical Pressure	5 046 kPa; 50.46 bar; 49.8 atm; 731.9 psia
Critical Volume	3.700 dm^3/kg
Critical Density	0.270 kg/dm^3
Critical Compressibility Factor	0.275
Latent Heat of Fusion @ −90.7 °C	1 088.26 kJ/mol; 19.4 kJ/kg
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	75.14 J/(mol·°K)
Molar Specific Heat, Liquid @ 12 °C	106.32 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 12.5 °C	0.008 30 mPa·s; 0.008 30 $mN·s/m^2$; 0.008 30 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.014 81 W/(m·°K) 35.4 × 10^{-6} cal·cm/(s·cm^2·°C)
Refractive Index Liquid @ Saturation Pressure, n_D @ 25 °C	1.362

Description

Cyclobutane is a colorless, flammable, nontoxic gas.

Uses

Cyclobutane is primarily for physicochemical studies of the four-membered ring.

Toxicity

Cyclobutane is considered to be nontoxic. In high concentrations, it may produce slight anesthetic effects.

Precautions in Handling and Storage

The hazards associated with the handling of cyclobutane are due to its extreme flammability. Store and use cyclobutane in a well-ventilated area away from heat and all ignition sources such as flames and sparks. Never use a flame to detect cyclobutane leaks, use soapy water. Do not use cyclobutane around sparking motors and other non-explosion-proof equipment. Do not store reserve stocks of cyclobutane cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all equipment and lines used with cyclobutane.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

All fittings and valves should be painted with soap water solution to detect leaks which will be indicated by bubble formation. Never use a flame to detect leaks.

Disposal of Leaking Cylinders

Cylinders of cyclobutane which develop leaks that can not be corrected by normal procedures may be disposed of by the procedure described in Appendix II-A.

Materials of Construction

Since cyclobutane is a noncorrosive gas, any common or commercially available metal may be used. However, piping systems or vessels to contain cyclobutane should be designed

to have a working pressure as specified by competent engineers using a safety factor conforming to the ASME code for pressure piping.

Shipping Regulations

Cyclobutane is classified by the DOT as a flammable, compressed gas and is shipped with the required "Red Gas Label".

Chemical Preparation

The preparation of cyclobutane has always been effected through intermediates that are difficult to prepare. Thus, it has been obtained by hydrogenation of cyclobutene over nickel catalysts at 100 °C; by converting cyclobutyl bromide to cyclobutylmagnesium bromide, followed by hydrolysis of the latter with water; by Huang-Minlon reduction of cyclobutanone, with hydrazine and potassium hydroxide in ethylene glycol; from cyclobutanecarboxylic acid via a Hundsdiecker reaction.

Chemical Properties

Cyclobutane is considerably more reactive than butane, but less reactive than cyclopropane. It is inert to permanganate or to ozone and is stable at ambient temperatures to bromine and hydrogen iodide. The ring can be opened by hydrogenation, but this requires more drastic conditions (Ni catalyst, 200 °C) than is required to open the cyclopropane ring (Ni catalyst, 120 °C).

Thermodynamic and Detailed Physical Data

Molecular Structure

The cyclobutane ring is a strained one, with C—C and C—H bond lengths of 1.568 × 10^{-10} m (1.568 Å) and 1.096 × 10^{-10} m (1.096 Å), respectively, and H—C—H bond angles of 114°. Various physical measurements suggest that the equilibrium configuration for cyclobutane is one with a nonplanar skeleton (D_{2d} symmetry), but that the barrier hindering inversion of the molecule is sufficiently low so that even at ordinary temperatures an appreciable number of the molecules obey D_{4h} selection rules.

Infrared Spectrum

For the infrared spectra of gaseous and liquid cyclobutane see Figure 1.

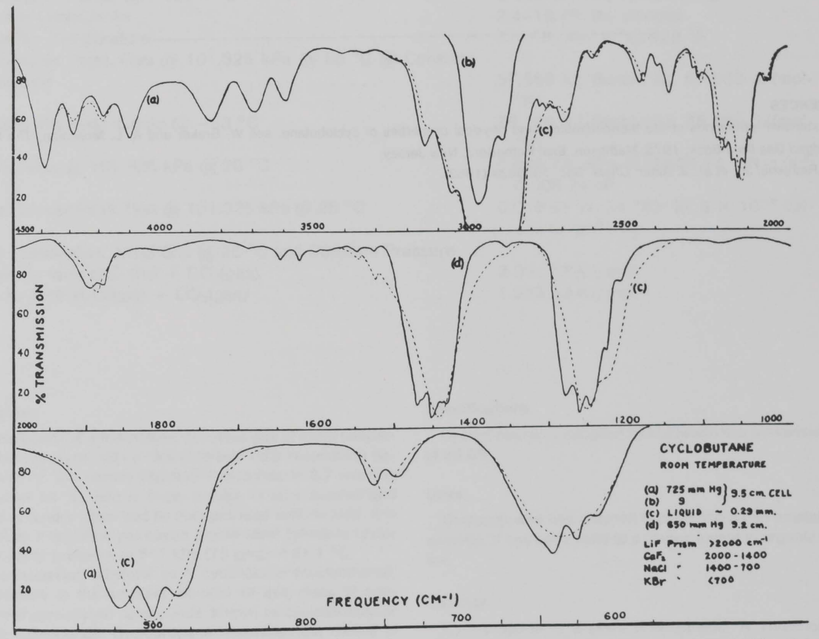


Fig. 1. Infrared spectra of cyclobutane. The optics used were as indicated in the figure, except that for the liquid spectrum NaCl optics were used below 1 400 cm^{-1} and CaF_2 optics above 1 400 cm^{-1} (2).

CYCLOBUTANE

Vapor Pressure (2)

The vapor pressure of liquid cyclobutane from −60 °C to 12.5 °C is represented by the following equation: $\log_{10}p = 24.669\,07 - \frac{1\,912.146}{T} - 6.892\,57\,\log_{10}T + 0.002\,913\,9T$

in which p = cmHg and T = °K.

Vapor pressure values obtained by this equation correspond very close to the following experimental values.

Temperature, °C	Vapor Pressure kPa	mbar	mmHg = torr
−59.93	2.497	24.97	18.73
−56.13	3.242	32.42	24.32
−49.00	5.172	51.72	38.79
−45.92	6.302	63.02	47.27
−33.86	12.711	127.11	95.34
−27.26	18.025	180.25	135.20
−20.42	25.382	253.82	190.38
−15.82	31.541	315.41	236.58
−10.31	40.475	404.75	303.59
−3.06	55.229	552.29	414.25
5.30	77.235	772.35	579.31
12.20	100.15	1 001.5	751.22
12.51	101.32	1 013.2	760.00

Latent Heat of Vaporization, ΔHv Temperature, °C	ΔHv, J/mol
−10	26.121
0.0	25.397
12.5	24.188
20.0	22.979

Thermodynamic Properties of Cyclobutane As Ideal Gas @ 25 °C (2)

Heat Capacity, C_p°	72.22 J/(mol·°K)
Entropy, S°	265.39 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_0^\circ)/T$	219.12 J/(mol·°K)
Enthalpy Function $(H_{298}^\circ - H_0^\circ)/T$	46.32 J/(mol·°K)

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of cyclobutane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] G. W.Rathjens, Jr., *et al., J. Amer. Chem. Soc.* 75, 5634 (1953).

CYCLOPROPANE

(Synonym: Trimethylene)
(Formula: C_3H_6)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.042 081 kg
One Mole of C_3H_6	0.042 081 kg
Specific Volume @ 21.1 °C, 101.325 kPa	574.3 dm^3/kg; 9.2 ft^3/lb
Vapor Pressure @ 21.1 °C	618.4 kPa; 6.18 bar; 89.65 psia; 6.10 atm
Boiling Point @ 101.325 kPa	240.35 °K; −32.8 °C; −27.0 °F
Freezing Point	145.73 °K; −127.4 °C; −261.3 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	1.751 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	1.453
Density, Liquid @ −40 °C	0.689 kg/l
Critical Temperature	397.81 °K; 124.7 °C; 256.4 °F
Critical Pressure	5 495 kPa; 54.95 bar; 54.23 atm; 797 psia
Critical Volume	4.040 dm^3/kg
Critical Density	0.248 kg/dm^3
Critical Compressibility Factor	0.282
Latent Heat of Fusion @ −127.4 °C	5.443 kJ/mol; 129.3 kJ/kg
Flammable Limits in Air	2.4–10.4% (by volume)
Autoignition Temperature	771 °K; 497.8 °C; 928 °F
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	57.559 kJ/(kmol·°K); 57.559 J/(mol·°K)
Molar Specific Heat, Liquid @ −53 °C	78.199 kJ·(kmol·°K); 78.199 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.008 74 mPa·s; 0.008 74 $mN·s/m^2$; 0.008 74 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.015 61 W/(m·°K); 37.3 × 10^{-6} cal·cm/(s·cm^2·°C)
Heat of Combustion, Ideal Gas @ 25 °C and Constant Pressure	
Gross, to form H_2O (liq) + CO_2(gas)	2 091.37 kJ/mol
Net, to form H_2O(gas) + CO_2(gas)	1 959.33 kJ/mol

Description

Cyclopropane is a flammable, colorless gas at room temperature and pressure, with a characteristic odor resembling petroleum ether. It is readily liquefied. It dissolves in 2.7 volumes of water at 15 °C, and is freely soluble in ethyl alcohol and ether. It is readily absorbed by concentrated sulfuric acid. It is shipped as a liquefied petroleum gas in steel cylinders under its own vapor pressure of 517 kPa (75 psig) at 21.1 °C.

Not considering ethylene as a cycloalkane (cycloethane), cyclopropane is the smallest member of this class of nonbenzenoid carbocyclic compounds, known as cycloalkanes or alicyclic compounds. Cyclopropane resembles the olefins in reactivity. It is not as reactive as ethylene but it is more reactive than cyclobutane, the reactivity being associated with ring strain and C—C bond strengths.

Specifications

Cyclopropane as supplied by Matheson has a minimum purity of 99.0%.

Uses

Cyclopropane has attained importance as an inhalation anesthetic. It has been used to a limited extent in organic synthesis.

Toxicity

Cyclopropane is a general anesthetic. A Threshold Limit Value of 400 ppm is suggested for cyclopropane (concentration in air to which nearly all personnel may be repeatedly exposed, day after day, without adverse effects).

Effects In Man (2)

Cyclopropane is a general anesthetic and depending on the concentration and time of exposure, symptoms such as rapid respiration, diminished mental alertness, muscular incoordination, nausea, vomiting and loss of consciousness may occur.

Contact of the liquid form of cyclopropane with the skin can cause frostbite.

First Aid Treatment (2)

Inhalation

If the subject is conscious and becomes aware of any of the above symptoms, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration if needed and oxygen simultaneously. Treat symptomatically thereafter.

Skin Contact

In case of skin contact with the liquid form of cyclopropane, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The hazards associated with the handling of cyclopropane are due to its extreme flammability. Store and use cyclopropane in a well-ventilated area away from heat and all ignition sources such as flames and sparks. Never use flames to detect cyclopropane leaks, use soapy water. Do not use cyclopropane around sparking motors and other non-explosion-proof equipment. Do not store reserve stocks of cyclopropane cylinders with cylinders containing oxygen, chlorine or other highly oxidizing or flammable materials. Ground all equipment and lines used with cyclopropane.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

All fittings and valves should be painted with soap water solution to detect leaks which will be indicated by bubble formation. Never use a flame to detect leaks.

Disposal of Leaking Cylinders

Cylinders of cyclopropane which develop leaks that cannot be corrected by normal procedures may be disposed of by the procedure described in Appendix II-A.

It is also possible to absorb the cyclopropane, by introducing it at a moderate rate, into concentrated sulfuric acid.

Materials of Construction

Since cyclopropane is a noncorrosive gas, any common or commercially available metal may be used. However, piping systems or vessels to contain cyclopropane should be designed to have a working pressure as specified by competent engineers using a safety factor conforming to the ASME code for pressure piping.

Cylinder and Valve Description

DOT approved cylinders containing cyclopropane are usually of the low pressure type having a rated service pressure of 1 034 kPa (150 psig) or more. Cylinders of cyclopropane are equipped with valves having Compressed Gas Association (CGA) valve outlet No. 510, the approved standard connection with a thread size of 0.885 inch diameter, left-hand internal threads accepting a bullet-shaped nipple. (See Figure 1 for an

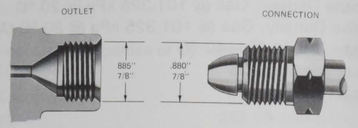


Fig. 1. CONNECTION 510 .885"-14 LH INT. accepting a Bullet Shaped Nipple

illustration of the valve outlet and its mating connection). This valve is standard for all liquefied petroleum gases. Valves used in this service by Matheson are of the diaphragm type and contain no packing.

Lecture bottles have a special 5/16"-32 threads per inch female outlet, and a 3/16"-18 threads per inch male dual valve outlet.

Safety Devices

A number of different safety devices are permitted on cylinders containing cyclopropane. The most commonly used safety device, which is used by Matheson, is the spring-loaded safety relief valve. If cylinder pressure becomes dangerously high (usually due to overheating) the device will open at about 2 586 kPa (375 psig) and release gas until the pressure again returns to a safe level.

Recommended Controls

Automatic Pressure Regulator

Matheson supplies single stage regulator Model 1P-510 for cyclopropane service. The regulator has a delivery pressure range of 28–240 kPa (4–35 psig). It has a brass body with brass internal parts plus a neoprene diaphragm and neoprene seat. No cylinder pressure gauge is necessary in this regulator since it would not indicate cylinder content but only vapor pressure which will remain constant as long as any liquid remains in the cylinder. Cylinder content should be determined by weighing. The Matheson Cylinder Scale Model 8510 is ideal for this purpose.

Accurate low pressure regulation of cyclopropane may be obtained with Matheson low pressure regulator Model 70-510. The regulator has a delivery pressure range of 3.4–34.5 kPa (0.5–5 psig). It is constructed of an oversize pancake body of die cast aluminum and a Buna N diaphragm.

To prevent suckback of foreign materials, a check valve is recommended for use with the above recommended regulators.

Matheson

Manual Controls

Matheson needle valve Model 50-510, a brass bar stock valve, is available for direct connection to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as serrated hose end, 1/4" compression fitting or 1/4" NPT male or female pipe. It is used mainly for intermittent flow control directly from the cylinder, but it requires constant attention by the user. It will not effectively control pressure and should not be used where pressure control is necessary. Brass needle valve Model 31B is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ±1.2%.

Shipping Regulations

Cyclopropane is shipped under DOT regulations as a flammable, liquefied compressed gas, taking a "Red Gas Label".

Chemical Preparation

Cyclopropane is prepared by treating 1,3-dichloropropane in ethyl alcohol with zinc in the presence of catalysts.

Chemical Properties

Bromine and iodine convert cyclopropane into the corresponding 1,3-dihalopropanes. Thermal chlorination gives chiefly chlorocyclopropanes contaminated with some allyl chloride. This impurity may be avoided by photochemical reactions. Iodine bromide reacts slowly with cyclopropane. Hydrogen halides cleave the cyclopropane ring giving propyl halides. Cyclopropane is inert to ozone and cold potassium permanganate solution. Pyrolysis of cyclopropane at 400–500 °C gives chiefly propylene; higher temperatures result in the formation of hydrogen, ethylene, saturated hydrocarbons and carbon. Lower temperatures can be used to convert cyclopropane to propylene if metallic catalysts are employed. Cyclopropane can be catalytically reduced to propane.

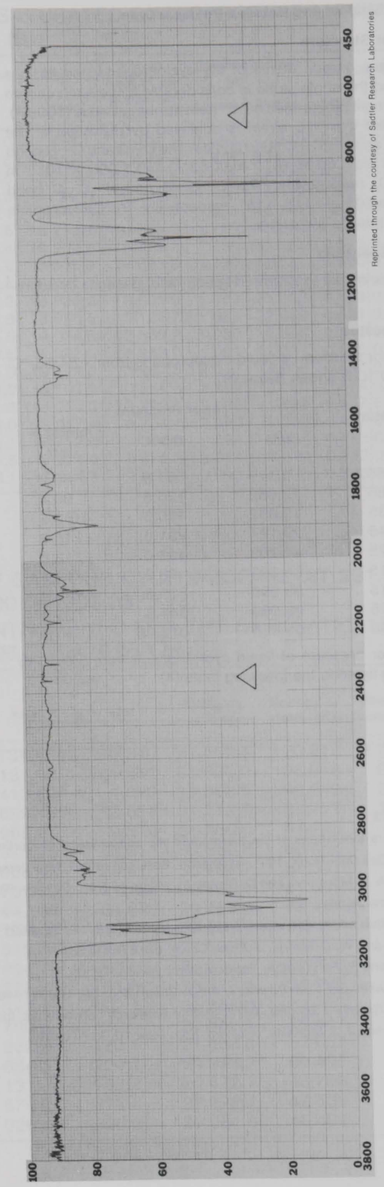


Fig. 2. Infrared spectrum of gaseous cyclopropane in the 3 800–450 cm^{-1} range; 10 cm path length cell, with KBr windows; cell pressure: 6.666 kPa (50 mmHg) (7).

Matheson

Thermodynamic and Detailed Physical Data

Molecular Structure

The three carbon atoms of the cyclopropane ring lie in a plane, and the angle strain is considerable since each carbon valence angle is deformed 49.5° from its normal value (109.5°). Some relief from the strain is achieved by distortion of the H—C—H and H—C—C bond angles. The C—C and C—H bond distances are 1.53×10^{-10} m (1.53 Å) and 1.090×10^{-10} m (1.090 Å), respectively. The C—C—C and H—C—C bond angles are 60° and 116–118°, respectively. The cyclopropane molecule has D_{3h} symmetry.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous cyclopropane.

Vapor Pressure

The vapor pressure of liquid cyclopropane from −84.55 °C to −32.80 °C is shown below (3).

Temperature, °C	Vapor Pressure kPa	mbar	mmHg = torr
−84.55	6.159	61.6	46.2
−74.85	12.052	120.5	90.4
−67.35	19.052	190.5	142.9
−59.45	29.184	291.8	218.9
−52.75	41.703	417.0	312.8
−47.15	55.209	55.21	414.1
−38.15	83.060	830.6	623.0
−34.25	98.099	981.0	735.8
−32.80	101.325	1 013.25	760.0

The vapor pressure of liquid cyclopropane from 3.0 °C to 124.6 °C is listed in the following table (4).

Temperature, °C	Vapor Pressure kPa	bar
3.00	241.2	2.41
10.92	406.3	4.06
16.78	537.0	5.37
32.42	792.4	7.92
43.28	1 231.1	12.31
52.42	1 545.2	15.45
61.32	1 688.1	16.88
71.42	2 261.6	22.62
81.19	2 613.2	26.13
91.10	3 052.9	30.53
101.31	3 459.2	34.59
110.02	4 152.2	41.52
124.65	4 586.0	45.86
150.34 (C.T.)	5 494.9	54.95 (C.P.)

For additional vapor pressure data, see Figure 3 and Table 1.

Latent Heat of Vaporization, ΔHv

Temperature, °C	ΔHv, kJ/mol
−73.15	21.959
−53.15	20.997
−32.80	20.054
−13.15	19.068
6.85	17.964
26.85	16.737

Thermodynamic Properties of Cyclopropane as Ideal Gas @ 25 °C

Heat Capacity, C_p°	56.066 J/(mol·°K) (5)
Entropy, S°	237.82 J/(mol·°K) (6)

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of cyclopropane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 197* Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, 1977, pp. 11–16, Matheson, Lyndhurst, New Jersey.

[3] G. G. Haselden and P. Snowden, *Trans Faraday Soc. 58*, 1515 (1962).

[4] H. S. Booth and W. C. Morris, *J. Phys. Chem. 62*, 875 (1958).

[5] K. A. Kobe and R. Pennington, *Petrol. Refiner 29*, 93 (1950).

[6] R. A. Ruehrwein and T. M. Powell, *J. Amer. Chem. Soc. 68*, 1063 (1946).

[7] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[8] D. C.-K. Lin and J. J. McKetta, *J. Chem. Eng. Data 16*, 416 (1971).

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED CYCLOPROPANE LIQUID AND VAPOR (8)

Temperature °K	Temperature °F	Pressure kPa	Pressure atm	Entropy J/(mol·°K) Liquid	Entropy J/(mol·°K) Vapor	Enthalpy J/mol Liquid	Enthalpy J/mol Vapor	Latent Heat of Vaporization J/mol	Specific Volume dm³/kg Liquid	Specific Volume dm³/kg Vapor	Density kg/dm³ Liquid	Density kg/dm³ Vapor
291.67	65.33	605.291	5.974	0.000	59.669	0.0	17 401.3	17 401.3	1.593	77.910	0.628	0.012 84
297.22	75.33	706.437	6.972	1.620	58.982	508.6	17 557.8	17 049.2	1.614	69.919	0.620	0.014 30
302.78	85.33	819.442	8.087	3.416	58.507	1 036.8	17 714.3	16 677.5	1.635	62.178	0.612	0.016 08
308.33	95.33	944.995	9.326	5.176	58.049	1 574.8	17 880.6	16 305.8	1.658	54.912	0.603	0.018 21
313.89	105.33 1	083.99	10.70	6.937	57.627	2 142.1	18 046.9	15 904.8	1.683	48.294	0.594	0.020 71
319.44	115.33 1	237.26	12.21	8.715	57.239	2 709.5	18 213.1	15 503.6	1.710	42.376	0.585	0.023 60
325.00	125.33 1	405.70	13.87	10.564	56.940	3 296.4	18 369.6	15 073.2	1.739	37.157	0.575	0.026 91
330.56	135.33 1	590.14	15.69	12.360	56.606	3 912.6	18 535.9	14 623.3	1.770	32.581	0.565	0.030 69
336.11	145.33 1	791.67	17.68	14.173	56.289	4 548.4	18 702.2	14 153.8	1.804	28.586	0.554	0.034 98
341.67	155.33 2	011.20	19.85	16.004	55.989	5 184.2	18 839.2	13 655.0	1.842	25.102	0.543	0.039 84
347.22	165.33 2	249.90	22.20	17.818	55.637	5 829.8	18 956.5	13 126.7	1.883	22.056	0.531	0.045 34
352.78	175.33 2	508.86	24.76	19.596	55.215	6 465.6	19 034.8	12 569.2	1.930	19.390	0.518	0.051 57
358.33	185.33 2	789.41	27.53	21.375	54.739	7 140.5	19 093.5	11 953.0	1.981	17.037	0.505	0.058 70
363.89	195.33 3	092.71	30.52	23.258	54.281	7 835.0	19 122.8	11 287.8	2.040	14.958	0.490	0.066 85
369.44	205.33 3	420.28	33.76	25.125	53.700	8 549.0	19 103.3	10 554.3	2.109	13.104	0.474	0.076 31
375.00	215.33 3	773.64	37.24	27.150	53.067	9 331.5	19 054.3	9 722.8	2.190	11.424	0.457	0.087 54
380.56	225.33 4	154.30	41.00	29.280	52.274	10 163.0	18 917.4	8 754.4	2.290	9.889	0.437	0.101 12
386.11	235.33 4	564.19	45.05	31.727	51.324	11 141.1	18 712.0	7 570.9	2.423	8.434	0.413	0.118 57
391.67	245.33 5	005.18	49.40	34.668	49.915	12 334.5	18 311.0	5 976.5	2.621	6.979	0.382	0.143 29
397.22	255.33 5	479.26	54.08	40.654	48.031	14 770.1	17 694.7	2 924.6	3.093	5.128	0.323	0.195 01

Table 2. THERMODYNAMIC PROPERTIES OF GASEOUS CYCLOPROPANE AT 291.67 °K (65.33 °F) AND 475.00 °K (395.33 °F)(8)

REFERENCE STATE: ENTHALPY = 0 AND ENTROPY = 0 FOR THE SATURATED LIQUID AT 291.67 °K AND 605.3 kPa (6.053 bar)

Pressure kPa	Pressure atm	Temperature, 291.67 °K Enthalpy J/mol	Entropy J/(mol·°K)	Specific Volume dm³/kg
34.474	0.340	18 164.2	85.304	1 662.5
68.948	0.680	18 134.9	79.477	826.5
103.42	1.021	18 095.8	76.026	548.2
137.90	1.361	18 066.4	73.578	408.8
172.37	1.701	18 027.3	71.642	325.1
206.84	2.041	17 997.9	70.057	269.3
275.79	2.722	17 919.7	67.486	199.5
344.74	3.402	17 831.7	65.444	157.4
413.69	4.083	17 743.6	63.701	129.3
482.63	4.763	17 636.0	62.152	109.1
551.58	5.444	17 508.9	60:743	93.83

Pressure kPa	Pressure atm	Temperature, 475.00 °K Enthalpy J/mol	Entropy J/(mol·°K)	Specific Volume dm³/kg
34.474	0.340	31 555.1	120.218	2 718.7
137.90	1.361	31 506.2	108.616	677.3
413.69	4.083	31 359.5	99.249	223.5
689.48	6.805	31 212.7	94.777	132.3
965.27	9.526	31 066.0	91.748	93.83
1 378.95	13.61	30 850.8	88.456	64.61
2 068.43	20.41	30 498.7	84.547	41.92
2 757.90	27.22	30 136.8	81.607	30.55
3 447.38	34.02	29 755.3	79.177	23.71
4 136.85	40.83	29 364.0	77.047	19.15
5 515.81	54.44	28 503.3	73.279	13.43
6 894.76	68.05	27 427.3	69.599	9.976
8 273.71	81.66	26 273.1	66.096	7.610
10 342.1	102.1	25 255.8	62.785	5.386
13 789.5	136.1	22 869.1	56.447	3.593
17 236.9	170.1	21 538.8	52.662	2.932
20 684.3	204.1	20 873.7	50.408	2.628
24 131.6	238.2	20 472.7	48.788	2.447
27 579.0	272.2	20 228.1	47.538	2.325
31 026.4	306.2	20 061.8	46.499	2.236

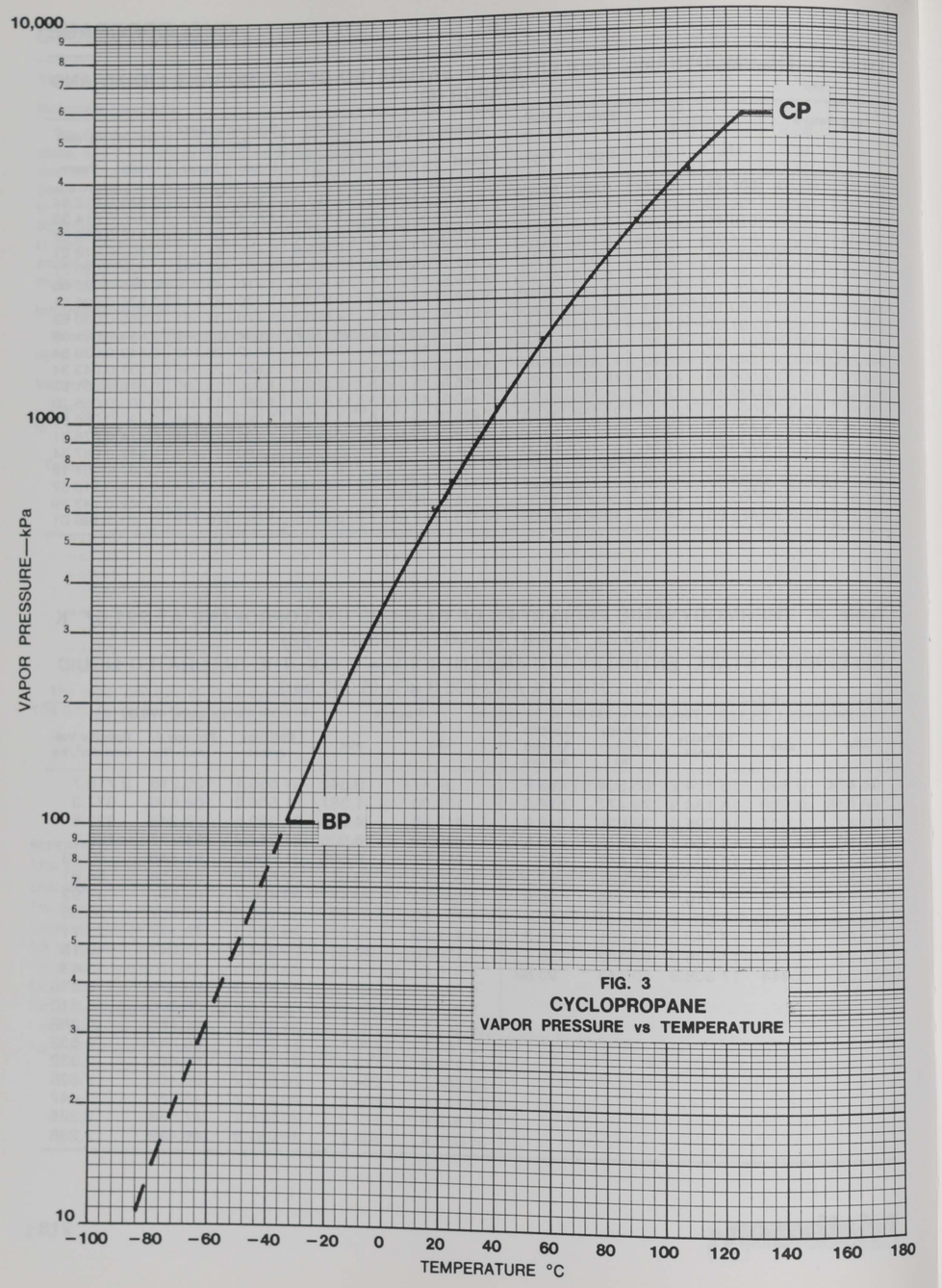


FIG. 3
CYCLOPROPANE
VAPOR PRESSURE vs TEMPERATURE

DEUTERIUM

(Formula: D_2 or $^2H_2$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.004 032 kg
One Mole of D_2	0.004 032 kg
Specific Volume @ 21.1 °C, 101.325 kPa	5 987 dm^3/kg; 95.9 ft^3/lb
Boiling Point @ 101.325 kPa, Normal Deuterium, 66.7% o-D_2	23.654 °K; −249.5 °C; −417.1 °F
Equilibrium Deuterium, 97.8° o-D_2	23.626 °K; −249.5 °C; −417.1 °F
Triple Point	
Normal Deuterium, 66.7% o-D_2	
Temperature	18.72 °K; −254.4 °C; −426.0 °F
Pressure	17.13 kPa; 171.3 mbar; 128.5 mmHg
Equilibrium Deuterium, 97.8% o-D_2	
Temperature	18.62 °K; −254.5 °C; −426.2 °F
Pressure	17.13 kPa; 171.3 mbar; 128.5 mmHg
Absolute Density, Gas @ 101.325 kPa @ 0 °C	0.180 kg/m^3
Density, Liquid, Equilibrium Deuterium @ −252.8 °C	0.169 kg/l
Critical Temperature	
Normal Deuterium	38.34 °K; −234.8 °C; −390.7 °F
Equilibrium Deuterium	38.25 °K; −234.9 °C; −390.8 °F
Critical Pressure	
Normal Deuterium	1 664.8 kPa; 16.65 bar; 241.5 psia; 16.43 atm
Equilibrium Deuterium	1 649.6 kPa; 16.50 bar; 239.2 psia; 16.28 atm
Critical Volume Equilibrium Deuterium	14.955 3 dm^3/kg
Critical Density Equilibrium Deuterium	0.066 8 kg/dm^3
Critical Compressibility Factor Equilibrium Deuterium	0.312
Latent Heat of Fusion, Equilibrium Deuterium @ −254.5 °C	196.94 J/mol; 47.07 cal/mol
Flammability Limits in Air	5–75% (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	29.204 J/(mol·°K); 6.980 cal/(mol·°C)
@ Constant Volume	20.878 J/(mol·°K); 4.990 cal/(mol·°C)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.40
Viscosity, Normal Deuterium @ 101.325 kPa @ 0 °C	0.010 1 mPa·s; 0.010 1 $mN·s/m^2$; 0.010 1 cP
Viscosity, Liquid, Equilibrium Deuterium @ −252.8 °C	0.040 mPa·s; 0.040 $mN·s/m^2$; 0.040 cP
Thermal Conductivity, Normal Deuterium @ 101.325 kPa @ 0 °C	0.1289 W/(m·°K); 308.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid, Equilibrium Deuterium @ −252.8 °C	1 264 W/(m·°K); 3.021 cal·cm/(s·cm^2·°C)
Surface Tension, Equilibrium Deuterium @ −252.8 °C	3.72 mN/m; 3.72 dyn·cm
Refractive Index, Normal Deuterium @ 101.325 kPa, n_D 25 °C	1.000 126 5
Dielectric Constant, Equilibrium Deuterium @ −252.8 °C	1.275

Description

Deuterium, a heavier stable isotope of ordinary hydrogen, is a colorless, odorless, nontoxic, flammable gas. It is shipped in high pressure steel cylinders at varying pressures depending on the quantity packaged.

Like molecular hydrogen, the diatomic deuterium molecule

shows ortho and para isomerism. At room temperature, deuterium exists as a 2:1 equilibrium mixture of ortho-para isomers. This is referred to as **normal deuterium**. Decreasing the temperature favors conversion to ortho deuterium. For example, at 20.4 °K the equilibrium mixture contains 97.8% ortho deuterium. This is referred to as **equilibrium deuterium**.

Specifications

Matheson supplies a C.P. grade of deuterium. This grade has a minimum isotopic purity of 99.5%.

Uses

Deuterium is used in tracer applications, in reaction rate studies, and exchange reaction studies, i.e., reactions in which one or more deuterium atoms trade places with light hydrogen atoms in some ion or molecule.

Toxicity

Deuterium is nontoxic but can act as an asphyxiant by displacing the necessary amount of air required to support life.

Precautions in Handling and Storage

The major hazards associated with the handling of deuterium is flammability. The following specific rules apply when handling deuterium:

1. Never use cylinders of deuterium in areas where flames, excessive heat or sparks may occur.
2. Utilize only explosion-proof equipment and spark-proof tools in areas where deuterium is handled.
3. Ground all equipment and lines used with deuterium.
4. Never use a flame to detect gas leaks—use soapy water.
5. Do not store reserve stocks of deuterium with cylinders containing oxygen, or with other highly oxidizing or combustable materials.
6. Do not place cylinders where they may become part of an electric circuit. When electric welding, precautions must be taken to prevent striking an arc against a cylinder.

In addition the general rules listed in Appendix I should be observed.

Leak Detection

Equipment to contain deuterium should be pretested with dry nitrogen.

Disposal of Leaking Cylinders

Cylinders of deuterium which develop leaks that can not be corrected by normal methods may be disposed of according to the procedure described in Appendix II-A.

Materials of Construction

Since deuterium is noncorrosive, no special materials of construction are required. However, any piping or vessels containing deuterium should be designed by competent engineers, using a safety factor conforming with the ASME code for pressure piping.

The handling of deuterium at elevated pressures and temperatures poses serious equipment problems, since possible deuterium embrittlement adds difficulties to normal equipment design.

Cylinder and Valve Description

Deuterium is packaged in DOT approved, high pressure steel cylinders. The cylinder valve outlet used by Matheson is a No. 350 connection, which is designated as standard for deuterium by the Compressed Gas Association (CGA). This valve outlet has a thread size of 0.825 inch diameter, with left-hand external threads accepting a round-shaped nipple. (See Figure 1 for an

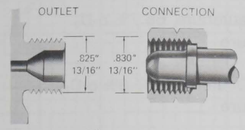


Fig. 1. CONNECTION 350 .825"-14 LH EXT. accepting Round Shaped Nipple

illustration of the valve outlet and its mating connection). Lecture bottles have a special 5/16"-32 threads per inch female outlet and a 9/16"-18 threads per inch male dual valve outlet.

Safety Devices

Matheson cylinders (except lecture bottles) containing deuterium have safety devices of the frangible disc type, backed up with fusible metal, melting at approximately 100 °C (212 °F). The safety device is an integral part of the cylinder valve and is situated opposite and slightly below the valve outlet.

Recommended Controls

Automatic Pressure Regulators

1. Single Stage Regulators

A single stage regulator will reduce cylinder pressure in one stage to a delivery pressure in a particular range, depending upon the design of the regulator and its spring load. A single stage regulator will show a slight variation in delivery pressure as cylinder pressure falls. The following recommended single stage regulators are available from Matheson for use with deuterium:

Model No	Delivery Pressure Range		
	kPa	bar (g)	psig
1L-350	28-550	0.28-5.5	4-80
1H-350	69-1 240	0.69-12.4	10-180
3320 (for lecture bottles)	28-410	0.28-4.1	4-60

2. Two Stage Regulator

This type of regulator performs the same function as the single stage regulator. However, greater accuracy and control of delivery pressure is maintained, and the delivery pressure does not vary as cylinder pressure falls. Automatic regulator Model 8-350 is recommended. The delivery pressure range of this regulator is 28–340 kPa (4–50 psig). A Model 9-350 regulator is also available. It has a delivery pressure range of 138–1 724 kPa (20–250 psig).

Manual Controls

Manual needle valves for direct attachment to the cylinder valve outlet are available. These types of controls are used mainly where intermittent flows are necessary, or where it is desired to control the flow of gas directly from the cylinder. This type of needle valve will allow control of extremely low flow rates, up to relatively large flow rates. However, pressure cannot be controlled with such a valve, and if a line or system becomes plugged, dangerous pressure can build up. The following manual type valves are recommended for use with deuterium: Model 50-350 or Model 52-350 with gauge to indicate tank pressure. These valves can be supplied with serrated hose-end, 1/4" compression fitting, or 1/4" NPT male or female outlets. Models 30AR and 31B are available for lecture bottle controls.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Shipping Regulations

Deuterium is shipped in high pressure steel cylinders as a flammable compressed gas, taking a DOT "Red Gas Label".

Commercial Preparation

Deuterium is prepared by electrolysis of heavy water (D_2O) which gives deuterium and oxygen.

Chemical Properties

Three isotopes of hydrogen are known. They have mass numbers of 1, 2 and 3, and are called hydrogen, deuterium (stable isotope), and tritium (unstable isotope), respectively.

Chemically, deuterium enters into all the reactions characteristic of ordinary hydrogen and forms completely equivalent compounds. Deuterium's larger mass and lower zero point energy (i.e., energy at absolute zero) give much different rates of reaction and different positions of equilibrium points in the same reaction. In general, deuterium reacts more slowly and less completely than ordinary hydrogen, and these properties characterize the behavior of corresponding compounds, as well as the elements themselves.

Thermodynamic and Detailed Physical Data

Infrared Spectrum

Diatomic molecules have only one vibration along the chemical bond. In the homopolar D—D molecule ($D_{\infty h}$ symmetry), the vibration is not infrared active but is Raman active. The observed fundamental vibrational frequency of D_2 is 2 993.44 cm^{-1}.

Vapor Pressure (2)

The vapor pressure of normal deuterium (66.7% o-D_2) and of equilibrium deuterium (97.8% o-D_2) are shown in the following table. The vapor pressure values have been calculated from the Antoine vapor pressure equation $\log_{10} p = A - B/(C + t)$, in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.128 25, 83.525 1 and 275.16 for normal deuterium, and 6.044 68, 79.588 and 274.680 for equilibrium deuterium.

Temperature, °K Normal Deuterium	Temperature, °K Equilibrium Deuterium	Vapor Pressure kPa	mbar	mmHg
17.703	17.690	10.67	106.7	80
18.167	18.147	13.32	133.3	100
19.068	19.043	20.00	200.0	150
19.758	19.730	26.66	266.6	200
20.325	20.295	33.33	333.3	250
20.811	20.779	40.00	400.0	300
21.621	21.589	53.33	533.3	400
22.290	22.258	66.66	666.6	500
22.866	22.835	79.99	800.0	600
23.375	23.345	93.33	933.3	700
23.470	23.440	95.99	960.0	720
23.563	23.534	98.66	986.6	740
23.609	23.580	99.99	1 000	750
23.654	23.626	101.325	1 013	760
23.699	23.671	102.66	1 027	770
23.744	23.716	103.99	1 040	780
23.832	23.804	106.66	1 067	800
24.249	24.223	119.99	1 200	900
24.634	24.610	133.32	1 333	1 000
25.328	25.308	159.99	1 600	1 200
26.230	26.210	199.98	2 000	1 500

The vapor pressure of normal deuterium from its boiling point to its critical point is shown below (3).

Temperature, °K	Vapor Pressure kPa	bar	atm
23.57	101.325	1.013	1.000 0
29.00	374.78	3.75	3.698 8
29.85	442.22	4.42	4.364 4
30.90	534.46	5.34	5.274 7
31.95	641.03	6.41	6.326 5
32.89	748.74	7.49	7.389 5
33.91	882.76	8.83	8.712 2
35.00	1 038.89	10.39	10.253
35.79	1 167.87	11.68	11.526
36.65	1 323.51	13.24	13.062
37.49	1 482.99	14.83	14.636
37.81	1 556.05	15.56	15.357
37.93	1 578.14	15.78	15.575
37.97	1 584.62	15.85	15.639
37.99	1 590.90	15.91	15.701
38.02	1 596.27	15.96	15.754
38.06	1 603.87	16.04	15.829
38.19	1 628.39	16.28	16.071
38. 34 (C.T.)	1 663.908	16.64	16.421 5

Latent Heat of Vaporization, Equilibrium Deuterium

@ −249.5 °C 1 229.80 J/mol; 293.93 cal/mol

DEUTERIUM

Thermodynamic Properties of Normal Deuterium As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	29.196 J/(mol·°K)
Entropy, S°	144.858 J/(mol·°K)
Free Energy Function, $(G_T^\circ - H_0^\circ)/T$	−116.186 J/(mol·°K)
Enthalpy Function $(H_T^\circ - H_0^\circ)/T$	28.740 J/(mol·°K)
Gibbs Energy of Formation, ΔG_f°	0.000 kJ/mol
Enthalpy of Formation ΔH_f° @ 0 °K	0.000 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of deuterium, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds, 1968*, Volume 1, Thermodynamic Research Center, Texas A & M University, College Station, Texas.

[3] A. S. Friedman, D. White, and H. S. Johnson, *J. Amer. Chem. Soc. 73*, 1320–1311 (1951).

[4] E. C. Kerr, *et al.*, *J. Amer. Chem. Soc. 73*, 282–284 (1951).

DIBORANE

(Formula: B_2H_6)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.027 668 kg
One mole of B_2H_6	0.027 668 kg
Boiling Point @ 101.325 kPa	180.31 °K; −92.8 °C; −135.1 °F
Freezing Point	108.29 °K; −164.9 °C; −264.8 °F
Absolute Density, Gas @ 101.325 kPa @ 0 °C	1.247 5 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 0 °C (Air = 1)	0.965
Density, Liquid @ Saturation Pressure @ −33.0 °C	0.341 kg/l
Critical Temperature	289.85 °K; 16.7 °C; 62.1 °F
Critical Pressure	4 004 kPa; 40.04 bar; 580.8 psia; 39.52 atm
Critical Volume	6.04 dm^3/kg
Critical Density	0.166 kg/dm^3
Critical Compressibility Factor	0.278
Latent Heat of Fusion @ −164.9 °C	4 473.1 J/mol; 1 068.1 cal/mol
Flammability Limits in Air	0.9–98.0% (by volume)
Autoignition Temperature	311–325 °K; 38–52 °C; 100–125 °F
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	2 065.1 J/(kg·°K)
@ Constant Volume	1 751.6 J/(kg·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.179
Molar Specific Heat, Saturated Liquid @ −103.1 °C	75.65 J/(mol·K)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.007 85 mPa·s; 0.007 85 mN·s/m^2; 0.007 85 cP
Viscosity, Liquid @ −109.2 °C	0.177 mPa·s; 0.177 mN·s/m^2 0.177 cP
Surface Tension @ 121.6 °C	18.6 mN/m; 18.6 dyn/cm

Description

Diborane is a colorless, flammable, toxic gas, with a sickly sweet odor. Undiluted diborane is received in cylinders containing 5 lb of diborane, refrigerated in dry ice. Because of its instability, no more than 0.100 kg (0.22 lb) per cylinder is shipped, pressurized with a diluent gas such as hydrogen, argon, nitrogen, or helium.

Specifications

Diborane used for the preparation of gas mixtures has a purity of at least 96%.

Uses

Catalyst for ethylenic, styrene, acrylic, and vinyl polymerization; rubber vulcanizer; reducing agent; flamespeed accelerator; intermediate for preparation of boron hydrides of higher molecular weight; for conversion of olefins to trialkyl boranes and primary alcohols; as a doping gas.

Effects in Man and Toxicity (2) (3)

Inhalation of small quantities of diborane may cause headache, nausea, weakness, tremors, convulsions, general lassitude, tightness of chest, coughing, respiratory difficulties, pulmonary edema and hemorrhage.

Diborane is an extremely toxic gas. Based on animal experiments, diborane toxicity appears to be comparable to phosgene, chlorine, fluorine, and arsine. The LC_{50} in humans by inhalation has been found to be 159 ppm/15 minutes. The 1979 ACGIH has established a Threshold Limit Value (TLV) of 0.1 ppm (0.1 mg/m^3) for diborane in air.

First Aid Treatment (2)

Remove the victim promptly to an uncontaminated atmosphere. Keep the victim warm (not hot) and quiet. Administer pure oxygen. If breathing is difficult or has stopped, give artificial respiration with simultaneous administration of oxygen.

Summon a physician immediately for anyone exposed to diborane.

Suggestions For Medical Treatment

Use intermittent positive pressure oxygen for pulmonary edema. If muscle spasm or muscle tremor is present, use barbituates to prevent convulsions. Treat anemia (if severe) by

transfusion. Treatment otherwise is symptomatic and supportive.

Precautions in Handling and Storage

Gas mixtures containing diborane should be handled only in a well-ventilated area, preferably a hood with forced ventilation, or in an area with a high normal air flow with provision for emergency ventilation at 30–60 air changes per hour. Only NIOSH-approved oxygen-generating apparatus or self-contained air supplied masks should be employed in diborane atmospheres. Air-supplied masks depending on a remote air supply should never be used unless the user is assured of escape from the contaminated area in the event of air-supply failure. Industrial gas masks should be used only for escape, and the wearer must immediately leave the contaminated area as soon as he smells diborane (inhalation of diborane temporarily deadens the olfactory senses so that concentrations above normal threshold concentration for smell can no longer be detected). Additional respiratory protective devices should be located in a convenient area near where diborane is being used for emergency use.

Do not store reserve stocks of diborane gas mixtures with cylinders containing oxygen or other highly oxidizing or flammable materials.

Ground all lines and equipment used with diborane or diborane mixtures containing flammable gas diluents.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Never use a flame to detect diborane leaks. The system should be pretested for leaks with nitrogen.

Disposal of Leaking Cylinders

Cylinders containing diborane which develop leaks that cannot be corrected normally may be disposed of as follows. Transfer the cylinder to a hood after donning an appropriate gas mask and neoprene gloves. Attach an appropriate regulator, with a long piece of flexible tubing attached to the outlet, to the cylinder valve outlet. Crack the cylinder valve and adjust a moderate rate of flow of diborane and introduce the gas into the bottom of a tall vessel containing water. Diborane is hydrolyzed by water to ultimately give hydrogen and boric acid.

Materials of Construction

Diborane does not attack any of the common metals of construction. Rubber and some greases and lubricants are attacked by it. Saran, polyethylene, Kel-F, Teflon, asbestos, graphite, and high-vacuum silicone grease are satisfactory. The design of diborane (undiluted) piping and equipment is highly specialized and must be handled by experienced engineers and safety and fire protection specialists.

Cylinder and Valve Description

Diborane gas mixtures are shipped in DOT approved, high pressure, steel cylinders. The cylinder valve outlet is the CGA standard, No. 350, which has a 0.825 inch left-hand external thread accepting a round-shaped nipple. It is commonly known as a standard hydrogen valve. Figure 1 shows a standard valve outlet and mating connection for diborane mixtures.

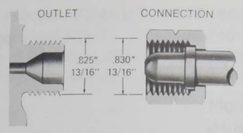


Fig. 1. CONNECTION 350 .825″-14 LH EXT. accepting Round Shaped Nipple

Safety Devices

Cylinders containing diborane gas mixtures are not equipped with safety devices. They should, therefore, be stored away from sources of heat to avoid the development of dangerous pressures within the cylinder.

Recommended Controls

High Purity Regulator Model 3503-350 is recommended for use with diborane gas mixtures. All parts in the gas stream, including the diaphragm, are of type 316 stainless steel. It has a Tefzel seat, a Model 4374 stainless steel diaphragm packless outlet valve, stainless steel delivery and cylinder pressure gauges, and Teflon gaskets. The helium leakage rate is certified not to exceed 2×10^{-10} cm^3 per second inboard. The delivery pressure range is 0–170 kPa (0–25 psig). The use of a Matheson Model 4774-350 Cross Purge is recommended for use with diborane mixtures.

Shipping Regulations

Diborane is presently classified by the DOT as a "Class A" poison flammable gas. In mixtures with nitrogen, helium, or argon it is shipped under required "Poison Gas and Green Labels". Mixtures of diborane and hydrogen are shipped under the required "Poison Gas and Red Gas Labels".

Chemical Preparation

Diborane is prepared by treating boron trichloride with lithium aluminum hydride in anhydrous diethyl ether and by treating boron trichloride with lithium hydride, sodium borohydride, or sodium trimethoxyborohydride in diethyl ether solution.

Chemical Properties

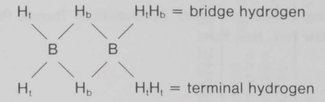
Diborane decomposes very slowly at room temperature to give hydrogen and higher boranes. The decomposition is accelerated at elevated temperatures. Lower pyrolysis temperatures favor the formation of tetraborane(10) and pentaborane(11) while higher temperatures favor the formation of pentaborane(9) and decaborane(14). Thus, relative yields of products can be preselected by adjustment to appropriate conditions. Diborane may remain for several days with air or oxygen at room temperature without inflaming; its ignition temperature is only slightly above room temperature. Diborane is hydrolyzed instantaneously by water at room temperature to ultimately give hydrogen and boric acid. Ammonia gives a stoichiometric compound with diborane: $B_2H_6 \cdot 2NH_3$. Diborane reacts with hydrocarbons or organoboron compounds to give alkyl and aryl boron compounds. Diborane reacts with metal alkyls to form metal borohydrides. Diborane reacts with strong electron pair donors to form borane addition compounds, e.g., $(CH_3)_3N{:}BH_3$, $(CH_3)_2O{:}BH_3$, $C_5H_5N{:}BH_3$

For detailed review of the chemistry of diborane, Reference 4 should be consulted.

Thermodynamic and Detailed Physical Data

Molecular Structure

The hydrogen-bridge structure of diborane, depicted below, has been established from its infrared, ultraviolet, and Raman spectra and confirmed by electron diffraction studies (5).



Parameters for this bridge model are as follows (6): bond distances:
B—B = 1.775 ± 0.004 Å (1.775 ± 0.004 × 10^{-10} m); B—H_t = 1.196 ± 0.016 Å (1.196 ± 0.016 × 10^{-10} m); B—H_b = 1.339 ± 0.013 Å (1.339 ± 0.013 × 10^{-10} m); H_t—B—H_t bond angle = 120.2 ± 1.6°. These constants agree well with those reported by Hedberg and Schomaker (5). Diborane has D_{2h} symmetry and a symmetry number of four (6).

Infrared Spectrum

The fundamental vibrational frequencies (in cm^{-1}) for the bridged B_2H_6 molecule are as follows (6): ν_1: 2 532; ν_2: 2 109; ν_3: 1 184; ν_4: 788; ν_5: 2 612; ν_6: 2 600; ν_7: 919; ν_8: 1 755; ν_9: 942; ν_{10}: 950; ν_{11}: 1 026; ν_{12}: 584; ν_{13}: 1 905; ν_{14}: 973; ν_{15}: 368; ν_{16}: 2 615; ν_{17}: 1 601; ν_{18}: 1 174.

The ν_5, ν_{11}, and ν_{13}–ν_{18} vibrations are infrared active, while the remaining vibrations are Raman active.

Vapor Pressure

The vapor pressure of liquid diborane up to its boiling point is shown below (7).

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
111.77	0.154 6	1.55	1.16
116.19	0.307 9	3.08	2.31
123.49	0.814 6	8.15	6.11
140.48	5.230	52.3	39.23
154.14	17.467	174.7	131.01
173.14	65.409	654.1	490.61
175.64	75.936	759.4	569.57
180.31 (calculated)	101.325	1 013.25	760.00

The vapor pressure of diborane above its boiling point is shown below (8).

Temperature, °K	Vapor Pressure kPa	bar	atm
199.88	268.917	2.69	2.654
208.82	390.203	3.90	3.851
218.58	560.631	5.61	5.533
229.80	819.922	8.20	8.092
239.81	1 123.90	11.24	11.092
249.84	1 489.17	14.89	14.697
288.42	3 661.07	36.61	36.132
289.85 (C.T.)	4 004.36	40.04	39.52 (C.P.)

These data as well as those below the boiling point may be represented by the following equation:

$$\log_{10} p = 8.125\,1 - 870.68/T - 0.002\,339T$$

in which p = mmHg and T = °K.

Latent Heat of Vaporization, ΔHv calculated (9)

Temperature, °K	ΔHv kJ/mol	kcal/mol
173.15	14.619	3.494
180.31	14.276	3.412 (7)
193.15	13.619	3.255
213.15	12.468	2.980
233.15	11.117	2.657
253.15	9.422	2.252
273.15	6.987	1.670

Thermodynamic Properties of Diborane As Ideal Gas @ 25 °C (6)

Heat Capacity, C_p°	58.099 J/(mol·°K)
Entropy, S°	233.086 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/T$	−233.086
Enthalpy Difference, $H_{298}-H_0^\circ$	12.150 kJ/mol
Enthalpy of Formation, ΔH_f°	41.003 kJ/mol
Free Energy of Formation, ΔF_f°	91.801 kJ/mol

For the thermodynamic properties of saturated diborane liquid and vapor, see Table 1.

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of diborane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, 1975, Matheson, East Rutherford, New Jersey.

[2] W. B. Deichmann and H. W. Gerarde, *Toxicology of Drugs and Chemicals*, 1969, pp. 137–138, Academic Press, Inc., New York, New York.

[3] D. I. Hurd, Chemistry of the Hybrides, 1952, pp. 212–215, John Wiley & Sons, Inc., New York, New York.

[4] G. W. Campbell, Jr., in Kirk-Othmer's **Encyclopedia of Chemical Technology**, 2nd edition, Volume 3, 1964, pp. 690–698, John Wiley & Sons, Inc., New York, New York.

[5] K. Hedberg and V. Schomaker, *J. Chem. Phys.* 73, 1482 (1951) and *J. Chem. Phys.* 22, 985 (1954).

[6] *JANAF Thermodchemical Tables*, 2nd edition, 1971, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[7] J. T. Clarke, E. B. Rifkin, and H. L. Johnston, *J. Amer. Chem. Soc.* 75, 781–785 (1953).

[8] E. B. Rifkin, E. C. Kerr, and H. L. Johnston, *J. Amer. Chem. Soc.* 75, 785–788 (1953).

[9] R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids*, 2nd edition, 1966, pp 147–148, McGraw-Hill Book Co., Inc., New York, New York.

[10] H. J. Galbraith and J. F. Masi in *Thermodynamic and Transport Properties of Gases, Liquids, and Solids*, Symposium on Thermal Properties, Sponsored by Amer. Soc. Mech. Engs., pp. 251–274, McGraw-Hill Book Co., Inc., New York, New York.

Matheson®

Matheson®

DIBORANE

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED DIBORANE LIQUID AND VAPOR (10)

Temperature		Pressure			Entropy J/(mol•°K)		Enthalpy Function H-E_0°/T J/(mol•°K)		Latent Heat of Vaporization kJ/kg	Specific Volume m^3/kg		Density kg/m^3	
°K	°F	kPa	Bar	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
130	−225.7	1.694	0.017	0.016 72	103.123	229.986	−93.229	33.636	596.1	0.002 08	22.989	481.7	0.043 5
140	−207.7	4.985	0.050	0.049 20	108.951	223.631	−80.976	33.702	580.3	0.002 12	8.333	471.5	0.120
150	−189.7	12.447	0.124	0.122 84	114.223	218.062	−70.527	33.732	565.2	0.002 17	3.571	461.2	0.280
160	−171.7	27.285	0.273	0.269 28	119.118	214.271	−61.441	33.712	550.3	0.002 22	1.724	450.6	0.580
170	−153.7	53.887	0.539	0.531 82	123.759	210.802	−53.412	33.630	534.8	0.002 27	0.909	439.9	1.10
180	−135.7	97.767	0.978	0.964 89	128.231	207.928	−46.217	33.479	518.5	0.002 33	0.526	428.8	1.90
190	−117.7	165.413	1.65	1.632 5	132.599	205.539	−39.691	33.255	500.9	0.002 40	0.323	417.4	3.10
200	−99.7	264.083	2.64	2.606 3	136.896	203.560	−33.711	32.957	481.9	0.002 47	0.208	405.7	4.80
210	−81.7	401.592	4.02	3.963 4	141.164	201.924	−28.178	32.581	461.2	0.002 54	0.141	393.4	7.10
220	−63.7	586.125	5.86	5.784 6	145.436	200.568	−23.017	32.120	438.4	0.002 63	0.097	380.4	10.3
230	−45.7	826.234	8.26	8.154 3	149.733	199.455	−18.159	31.561	413.3	0.002 73	0.069	366.7	14.4
240	−27.7	1 130.79	11.31	11.160	154.126	198.548	−13.540	30.877	385.3	0.002 84	0.050	351.8	20.0
250	−9.7	1 509.44	15.09	14.897	158.682	197.790	−9.086	30.025	353.4	0.002 98	0.037	335.2	27.2
260	8.3	1 972.80	19.73	19.470	163.527	197.142	−4.693	28.920	315.9	0.003 16	0.027	316.1	37.1
270	26.3	2 533.63	25.34	25.005	168.975	196.527	−0.169	27.386	268.9	0.003 42	0.020	292.6	51.0
280	44.3	3 207.85	32.08	31.659	175.841	195.820	4.961	24.938	202.2	0.003 85	0.014	260.0	73.3
289.85	62.1	4 004.36	40.04	39.520	193.782	193.782	15.305	15.305	0.000	0.006 03	0.006	165.8	165.8

DIBROMODIFLUOROMETHANE

(Synonym: Freon-12B2®)
(Formula: CBr_2F_2)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.209 82 kg
One Mole of CBr_2F_2	0.209 82 kg
Vapor Pressure @ 21.1 °C	82.7 kPa; 0.83 bar; 12 psia; 0.82 atm
Boiling Point @ 101.325 kPa	297.05 °K; 23.9 °C; 75.0 °F
Freezing Point	133.05 °K; -140.1 °C; -220.2 °F
Absolute Density, Gas @ 101.325 kPa @ 40 °C	8.171 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 40 °C (Air = 1)	7.244
Density, Liquid @ 15 °C	2.462 kg/l
Critical Temperature	471.35 °K; 298.2 °C; 388.8 °F
Critical Pressure	5 330 kPa; 53.30 bar; 773.0 psia; 52.6 atm
Critical Volume	0.957 dm^3/kg
Critical Density	1.045 kg/dm^3
Critical Compressibility Factor	0.273
Dipole Moment	2.27 × 10^{-30} C·m; 0.68 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	381.869 J/(kg·°K)
@ Constant Volume	342.184 J/(kg·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.116
Viscosity, Gas @ 101.325 kPa @ 23.9 °C	0.015 9 mPa·s; 0.015 9 mN·s/m^2; 0.015 9 cP
Viscosity, Liquid @ 23.9 °C	0.47 mPa·s; 0.47 mN·s/m^2; 0.47 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 23.9 °C	0.007 55 W/(m·°K); 18.04 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ 21.1 °C	0.115 9 W/(m·°K); 277 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 20 °C	17.8 mN/m; 17.8 dyn/cm

Description

Dibromodifluoromethane is a colorless, nonflammable, nontoxic liquid at temperatures below 24.5 °C. It is shipped as a liquid in small cylinders and lecture bottles.

Specifications

There are no purity specifications of dibromodifluoromethane but it conforms to the military specification MIL-D-4540 (USAF). This specification calls for the following requirements:

Item	Requirement
Specific Gravity @ 15 °/15 °C	2.270-2.310
Index of refraction, n^{15}	1.396 0-1.404 0
Distillation range, 1 atm (to 95%)	21.0-32.0 °C (max.)
Nonvolatile residue	0.02 g/100 ml (max.)
Free bromine and hydrobromic acid	to pass test
Sodium iodide in acetone test	to pass test
Cloud point	0 °C (max.)
Suspended matter	none
Sediment	none
Color	colorless
Odor, initial residual	none

Uses

Dibromodifluoromethane is useful as a fire extinguishing agent.

Toxicity

Dibromodifluoromethane has comparatively low toxicity. The approximate lethal concentration of dibromodifluoromethane for rats after 15 minutes exposure to the vapors is 54 000 ppm. The vapors exposed to 800 °C for one second tested on rats show an approximate lethal concentration of 1 850 ppm after 15 minutes exposure. It is classified by the Underwriters' Laboratories system of comparative toxicity as a Group 4 gas. This category includes those gases and vapors which in concentrations of about 2–2.5% for durations of exposure of about 2 hours are lethal or reproduce serious injury. The 1979 ACGIH Threshold Limit Value (TLV) for dibromodifluoromethane has been set at 100 ppm (860 mg/m^3).

First Aid Treatment

Inhalation

Remove the victim to an uncontaminated atmosphere, administer oxygen, and observe for premonitory signs of delayed

pulmonary edema. Subsequent treatment is symptomatic and supportive.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Leak Detection

Leaks of dibromodifluoromethane may be detected by applying soap water solution to the suspected points; leaks will be indicated by bubble formation. Leaks of dibromodifluoromethane in dark, confined or inaccessible spaces or locations may be located by means of a halide torch or lamp. The Matheson Leak Detector Model 8016 and 8017 is useful for leak detection.

Materials of Construction

Dry or wet dibromodifluoromethane does not affect copper or stainless steel at room temperature. Dry dibromodifluoromethane does not corrode aluminum, but wet dibromodifluoromethane causes pitting.

Cylinder and Valve Description

Dibromodifluoromethane is shipped in DOT approved, low pressure, steel cylinders. Cylinders containing dibromodifluoromethane are equipped with brass valves with the alternate standard Compressed Gas Association (CGA) outlet connection No. 660. The valve outlet has a thread size of 1.030 inches, with right-hand external threads with a flat seat and washer (see Figure 1). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet.

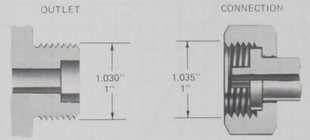


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

Safety Devices

No safety devices are required to be used in cylinders containing dibromodifluoromethane. Cylinders containing dibromodifluoromethane should, therefore, not be heated above 51.7 °C (125 °F) where dangerous hydrostatic pressures may build up.

Recommended Controls

Because of the low pressure, it is recommended that the cylinder valve be used either with a hose end with CGA connection No. 660, or with a flare fitting with connection CGA No. 660.

Shipping Regulations

Dibromodifluoromethane is shipped as a nonflammable liquid chemical in low pressure steel cylinders. No DOT label is required.

Commercial Preparation

Dibromodifluoromethane is obtained by vapor phase bromination of difluoromethane at elevated temperatures.

Thermodynamic and Detailed Physical Data

Molecular Structure

CBr_2F_2 has C_{2v} symmetry, and a symmetry number of two. The C—F bond distance is 1.33 × 10^{-10} m (1.33 Å), the C-Br distance 1.91 × 10^{-10} m (1.91 Å).

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous dibromodifluoromethane.

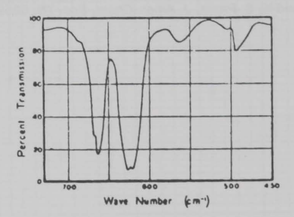


Fig. 2. Spectrum of Gaseous CBr_2F_2 in the region below 1 000 cm^{-1} obtained with a Beckman IR-2 spectrophotometer (KBr optics) (2).

Vapor Pressure (3)

The vapor pressure of dibromodifluoromethane between 221.75 °K and 284.35 °K is shown below:

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
221.75	2.67	26.7	20
230.65	4.60	46.0	34.5
244.05	10.07	100.7	75.5
266.35	30.93	309.3	232
273.15	50.80	508.0	381
284.35	64.53	645.3	484

These data are represented by the vapor pressure equation $\log_{10} p = 7.567 - 1\,387/T$, in which p = mmHg and T = °K. See Figure 3 for vapor pressure curve.

Temperature, °K	Latent Heat of Vaporization, ΔHv kJ/kg	ΔHv kcal/kg
273.15	133.206	31.837
297.05	126.625	30.264 (3)
303.15	125.030	29.883
323.15	119.047	28.453
348.15	111.073	26.547
373.15	101.897	24.354

DIBROMODIFLUOROMETHANE

Thermodynamic Properties of Dibromodifluoromethane as Ideal Gas @ 25 °C (4)			
Heat Capacity, C_p°	77.195 J/(mol·°K)	Entropy, S°	325.180 J/(mol·°K)
		Free Energy Function, $(F_{298}^\circ - H_0^\circ)/298$	−270.496 J/(mol·°K)
		Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	16.267 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of dibromodifluoromethane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] C. E. Decker, *et al.*, *J. Chem. Phys*, 21, 1781–1783 (1953).

[3] N. Davidson, *J. Amer. Chem. Soc.* 73, 467 (1951).

[4] E. Gelles and K. S. Pitzer, *J. Amer. Chem. Soc.* 75, 5259–5267 (1953).

Matheson

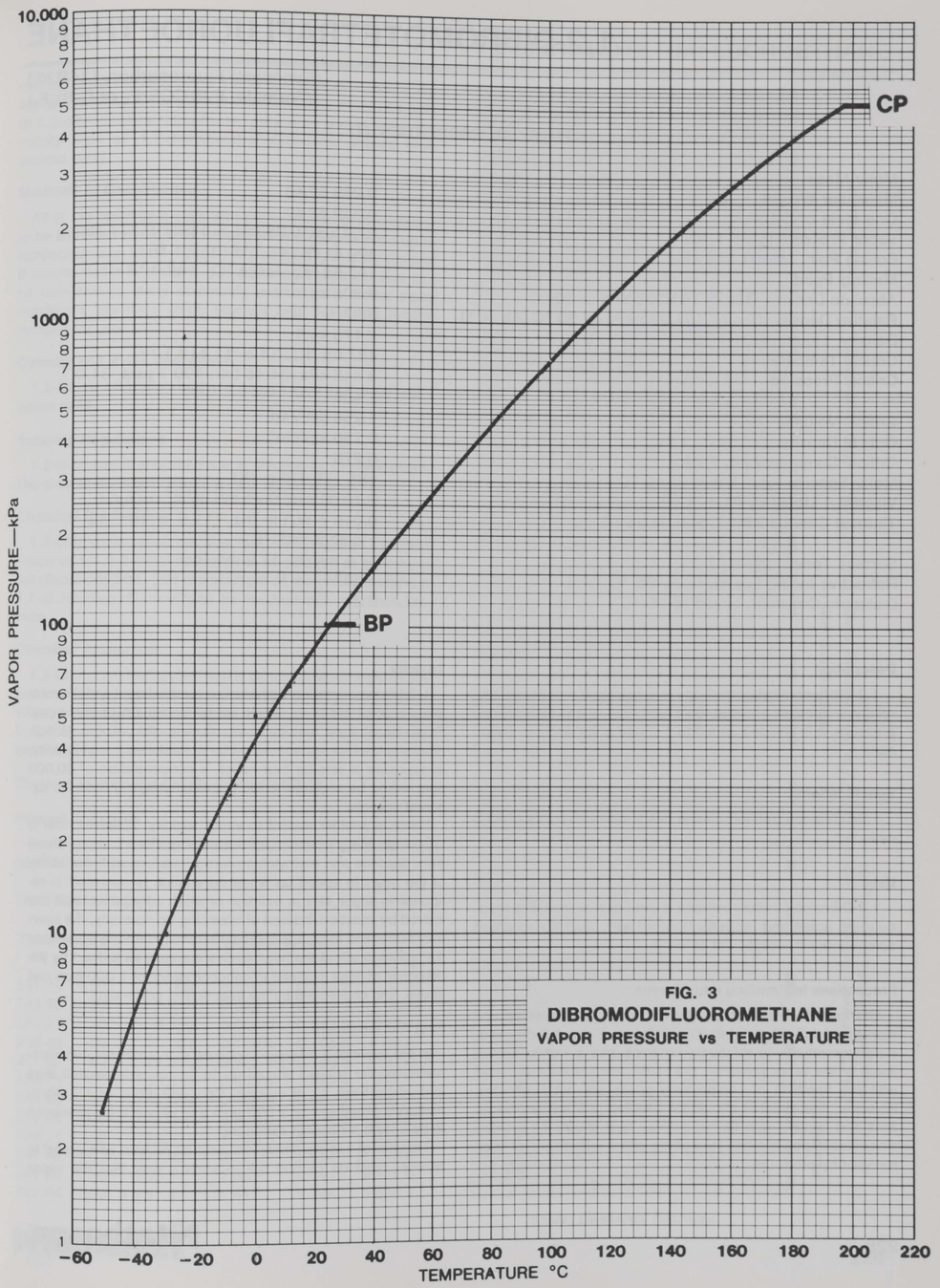


FIG. 3
DIBROMODIFLUOROMETHANE
VAPOR PRESSURE vs TEMPERATURE

1,2-DIBROMOTETRAFLUOROETHANE

(Synonym: Fluorocarbon-114B2®)
(Formula: $F_2BrCCBrF_2$ or $C_2Br_2F_4$)

PHYSICAL PROPERTIES (1)

Molar Mass	0.259 82 kg
Molecular Weight	0.259 82 kg
One Mole of C_2BrF_4	37.9 kPa; 0.38 bar; 5.5 psia; 0.374 atm
Vapor Pressure @ 21.1 °C	320.41 °K; 47.3 °C; 117.1 °F
Boiling Point @ 101.325 kPa	162.65 °K; -110.5 °C; -166.9 °F
Melting Point	9.805 kg/m^3
Absolute Density, Gas @ 101.325 kPa @ 50 °C	8.97
Relative Density, Gas @ 101.325 kPa @ 50 °C (Air = 1)	2.175 kg/l
Density, Liquid @ 21.1 °C	487.65 °K; 214.5 °C; 418.1 °F
Critical Temperature	3 445 kPa; 34.45 bar; 499.7 psia; 34.0 atm
Critical Pressure	1.266 dm^3/kg
Critical Volume	0.790 kg/dm^3
Critical Density	0.279
Critical Compressibility Factor	686.176 J/(kg·°K)
Molar Specific Heat, Liquid @ 10 °C	0.75 mPa·s; 0.75 mN·s/m^2 0.75 cP
Viscosity, Liquid @ 21.1 °C	0.046 7 W/(m·°K); 111.6 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ 25 °C	17.9 mN/m; 17.9 dyn/cm
Surface Tension @ 26.7 °C	1.367
Refractive Index, Liquid, n_D @ 25 °C	2.34
Dielectric Constant, Liquid @ 25 °C	

Description

1,2-Dibromotetrafluoroethane is a colorless, nonflammable, relatively nontoxic liquid at room temperature and atmospheric pressure. It is shipped as a liquid in one quart and one gallon cans.

Specifications

1,2-Dibromotetrafluoroethane has a minimum purity of 99.5 mole %.

Uses

1,2-Dibromotetrafluoroethane is used as a solvent, fire extinguishing agent and propellant (mixed with other fluorocarbon compounds) in insecticidal aerosols.

Precautions in Handling and Storage

The following rules should be followed in the handling and storage of 1,2-dibromotetrafluoroethane. Since 1,2-dibromotetrafluoroethane is relatively nontoxic and a nonflammable liquid of low vapor pressure, the usual precautions associated with the handling of compressed gases are not applicable. However, the material should be handled in a well-ventilated area and contact with flames or high heat should be avoided since decomposition can take place with the formation of toxic halogen by-products.

Toxicity

1,2-Dibromotetrafluoroethane is a volatile liquid and the most likely type of exposure would be by inhalation of the vapor. From the straight toxicity point of view, the vapors of 1,2-dibromotetrafluoroethane would be considered low in toxicity; in exposure of rats for four hours, a concentration of 50,000 ppm would be required to kill approximately 50% of the exposed animals.

There is another aspect to vapor toxicity, however, that is important. Many common solvent vapors (for example, those from gasoline and methylchloroform) interfere with the ability of the heart to speed up when adrenaline is secreted in response to anger, fear or exertion or when adrenaline is administered by injection. Instead of speeding up normally, the heart may flutter and stop. 1,2-Dibromotetrafluoroethane possesses the ability to affect the heart in this manner, as judged by the response of dogs exposed to concentrations of 1 000 ppm and above, and challenged by the injection of adrenaline.

First Aid Treatment

In the event of a massive exposure to 1,2-dibromotetrafluoroethane, the subject should go to an uncontaminated area and inhale fresh air or oxygen. Concentrations of 1,2-dibromotetrafluoroethane of 1 000 ppm and above are considered to be unsafe for human exposure.

Transfer of 1,2-dibromotetrafluoroethane from one vessel to another must be carried out in such a way that the vapor

Matheson

concentration remains below 1 000 ppm wherever people are exposed without respiratory protection. In the event of a spill of 1,2-dibromotetrafluoroethane, personnel should leave the vicinity until all 1,2-dibromotetrafluoroethane vapors have cleared away.

Materials of Construction

All of the common metals with the exception of zinc appear to be suitable for use with 1,2-dibromotetrafluoroethane up to temperatures of 121.1 °C (250 °F), especially in a dry system. If excess water is present, 1,2-dibromotetrafluoroethane can be corrosive to many commonly used metals. Under these conditions, stainless steel, titanium and nickel are recommended for use.

Cylinder and Valve Description

1,2-Dibromotetrafluoroethane is packaged in 1 quart and 1 gallon cans.

Shipping Regulations

1,2-Dibromotetrafluoroethane is shipped as a nonflammable chemical. It does not require a DOT shipping label.

Chemical Preparation

1,2-Dibromotetrafluoroethane has been prepared by bromination of 1,1,2,2-tetrafluoroethane, by addition of bromine to tetrafluoroethylene, and replacement of the chlorine atoms in 1,2-dichlorotetrafluoroethane by reaction with hydrogen bromide.

Chemical Properties

1,2-Dibromotetrafluoroethane is comparatively thermally stable. It is hydrolyzed very slowly by water at room temperature. When treated with zinc dust in acetic acid at below room temperature, 1,2-dibromotetrafluoroethane undergoes debromination to give tetrafluoroethylene.

Thermodynamic and Detailed Physical Data

Infrared Spectrum

See Figure 1 for the infrared spectrum of gaseous 1,2-dibromotetrafluoroethane.

Vapor Pressure (2)

Temperature °K	Temperature °F	Vapor Pressure kPa	Vapor Pressure bar	Vapor Pressure atm	Vapor Pressure mmHg
227.59	−50	1.034	0.010 3	0.010 2	7.76
244.26	−20	2.965	0.029 7	0.029 3	22.24
255.37	0	5.792	0.058 0	0.057 2	43.4
266.48	20	10.687	0.106 9	0.105 5	80.2
277.59	40	18.271	0.182 7	0.180 3	137.0
288.71	60	30.337	0.303 4	0.299 4	227.5
299.82	80	46.884	0.468 8	0.462 7	351.7
310.93	100	72.395	0.724 0	0.714 5	543.0
338.71	150	175.816	1.758	1.735	1 318.7
366.48	200	372.32	3.723	3.674	2 792.6
394.26	250	703.27	7.033	6.941	5 274.9
422.04	300	1 151.4	11.51	11.364	8 636.4

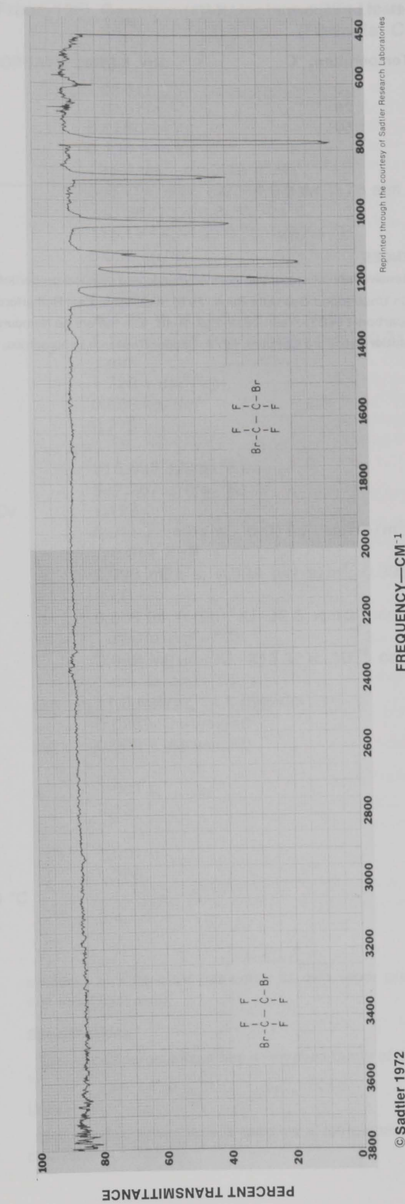


Fig. 1. Infrared spectrum of gaseous $C_2Br_2F_4$ in the frequency range 3 800-450 cm^{-1}; 10 cm path length; KBr optics; cell pressure: 0.667 kPa (5 mmHg) (3).

Matheson

1,2-DIBROMOTETRAFLUOROETHANE

Latent Heat of Vaporization, ΔHv (1)

Temperature, °C	ΔHv, kJ/kg
0	115.82
25	110.50
50	104.73
75	98.38
100	91.26

Standard Enthalpy of Formation, Gas @ 25 °C ..... −3 011.35 kJ/kg
−719.73 kcal/kg

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of 1,2-dibromotetrafluoroethane, see W. Baker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] **Fluorocarbon-114B2**, Freon Tech. Bull. B-4B, E. I. duPont de Nemours & Co., Inc., Wilmington, Delaware.

[3] **The Sadtler Standard Spectra**, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

DICHLORODIFLUOROMETHANE

(Synonym: Freon-12®, Genetron-12®, Isotron-12®, Ucon-12®)
(Formula: CCl_2F_2)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.120 914 kg
One Mole of CCl_2F_2	0.120 914 kg
Specific Volume @ 21.1 °C 101.325 kPa	195.4 dm^3/kg; 3.13 ft^3/lb
Vapor Pressure @ 21.1 °C	585 kPa; 5.85 bar; 84.9 psia; 5.78 atm
Boiling Point @ 101.325 kPa	243.36 °K; -29.8 °C; -21.6 °F
Freezing Point	115.15 °K; -158.0 °C; -252.4 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	5.056 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	4.2
Density, Liquid @ Saturation Pressure @ -45.6 °C	1.532 kg/l
Critical Temperature	384.95 °K; 111.8 °C; 233.2 °F
Critical Pressure	4 125 kPa; 41.25 bar; 598.3 psia; 40.71 atm
Critical Volume	1.729 1 dm^3/kg
Critical Density	0.558 kg/dm^3
Critical Compressibility Factor	0.279
Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	615.885 J/(kg·°K);
@ Constant Volume	547.267 J/(kg·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.127
Viscosity, Gas @ 101.325 kPa @ 4.4 °C	0.011 7 mPa·s; 0.011 7 $mN·s/m^2$; 0.011 7 cP
Viscosity, Liquid @ -40 °C	0.398 mPa·s; 0.398 $mN·s/m^2$; 0.398 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 10 °C	0.009 34 W/(m·°K); 22.3 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ -17.8 °C	0.090 W/(m·°K); 215.1 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 4.4 °C	11.8 mN/m; 11.8 dyn/cm
Solubility in Water @ 101.325 kPa @ 25 °C	0.028% (by weight)
Solubility of Water in Freon-12 @ 25 °C	0.009% (by weight)
Dielectric Constant	
Gas @ 29 °C, 50.7 kPa	1.001 6
Liquid @ 29 °C	2.13
Refractive Index, n_D	
Gas @ 26.7 °C, 101.325 kPa	1.001 0
Liquid @ 26.5 °C	1.285
Relative Dielectric Strength Gas @ 101.325 kPa @ 23.0 °C (Nitrogen = 1)	2.4

Description

Dichlorodifluoromethane is a colorless, nonflammable, relatively nontoxic gas at room temperature and atmospheric pressure. In concentrations of less than 20% (by volume), it is odorless; in higher concentrations, its odor is mild and somewhat ethereal and similar to that of carbon tetrachloride. Cylinders, truck cargo tanks, portable tanks, single-unit tank cars and ton multi-unit tanks are variously authorized for shipment of CCl_2F_2. It is readily liquefied and is reshipped in steel cylinders as a liquefied gas under its own vapor pressure of 484 kPa (70.2 psig).

Specifications

Dichlorodifluoromethane has a minimum purity of 99.0 mole %.

Uses

Dichlorodifluoromethane is used as a refrigerant and as a propellant in aerosols.

Toxicity and Effects in Man (2)

Dichlorodifluoromethane is practically nontoxic. It shows no toxic effects in guinea pigs in concentrations up to at least 20% (by vol.) for 2 hours exposure.

Inhalation of high concentrations of gas can cause such symptoms as dizziness, disorientation, incoordination, narcosis, nausea or vomiting. There appear to be no irreversible effects once the oxygen deficiency has been corrected.

Contact with liquid dichlorodifluoromethane can cause frostbite.

The 1979 ACGIH has established a 1 000 ppm (4950 mg/m^3) Threshold Limit Value (TLV) for dichlorodifluoromethane in air.

First Aid Treatment

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration if necessary and oxygen simultaneously. Treat symptomatically thereafter.

Skin Contact

In case of skin contact with liquid dichlorodifluoromethane, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Leak Detection

Leaks of dichlorodifluoromethane may be detected by applying soap water solution to suspected points; leaks will be indicated by bubble formation. Leaks of dichlorodifluoromethane in dark, confined or inaccessible spaces or locations may be located by means of a halide torch or lamp. The Matheson Leak Detector Models 8016 and 8017 may also be used to detect leaks of dichlorodifluoromethane.

Disposal of Leaking Cylinders

Cylinders containing dichlorodifluoromethane which develop leaks that cannot be corrected normally may be disposed of in the manner described in Appendix II-C.

Materials of Construction

Most of the commonly used metals (steel, cast iron, brass, copper, tin, lead, aluminum) may be used satisfactorily with dichlorodifluoromethane under normal conditions of use. At high temperatures, some of the metals may act as catalysts for the breakdown of the compound. The tendency of metals to promote thermal decomposition of dichlorodifluoromethane is in the following approximate order: silver > brass > bronze > aluminum > 1340 steel > copper > nickel > 18-8 stainless steel > inconel (least decomposition). Magnesium alloys and aluminum containing more than 2% magnesium are not recommended for use in systems containing dichlorodifluoromethane where water may be present.

In general, gasket materials should not contain natural rubber. Neoprene or Isoprene rubber, pressed fibers, including asbestos, with a number of insoluble binders, and metallic gaskets may be used.

Cylinder and Valve Description

Dichlorodifluoromethane is shipped in DOT approved, low pressure steel cylinders, having a rated service pressure of 1 550 kPa (225 psig) or more. Cylinders of dichlorodifluoromethane are equipped with brass values with the approved alternate Compressed Gas Association (CGA) outlet connection No. 660. The valve outlet is 1.030 inches in diameter, with right-hand external threads, used with a flat seat and washer (see Figure 1 for an illustration). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet and a 9/16"-18 threads per inch male dual valve outlet.

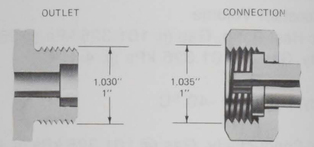


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders of dichlorodifluoromethane contain fusible metal plugs, melting at about 73.9 °C (165 °F), as safety devices. Cylinders over 30 inches long (exclusive of the neck) require this device in both ends of the cylinder.

Recommended Controls

Automatic Pressure Regulators

Regulators Model 1P-660 and Model 1L-660 are recommended for use with dichlorodifluoromethane. The regulators have delivery pressure ranges of 28-240 kPa (4–35 psig) and 28-550 kPa (4–80 psig), respectively. They are constructed of brass bodies with neoprene rubber diaphragms and neoprene seats. Regulator Model 1L-660 has a cylinder pressure gauge while the Model 1P-660 regulator does not have one. No cylinder pressure gauge is really necessary since it will not indicate cylinder content but only vapor pressure which will remain constant as long as liquid remains in the cylinder. Cylinder contents are determined by weight. To prevent suckback of foreign materials into the regulator, a check valve is recommended for use with the regulator.

Satisfactory low pressure regulation over the ranges 2-15 inches water column to 3.4-34.5 kPa (0.5–5.0 psig) can be obtained with Matheson Model 70 low pressure regulators, Models 70B and 70, respectively. The regulator has an oversize, pancake body of die cast aluminum with a Buna N diaphragm.

Manual Controls

Matheson needle valve Model 50-660, a brass bar stock valve, is available for direct connection to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, 1/4" compression fitting, or 1/4" NPT male or female pipe. It should be used only where manual flow control is required, but it requires close supervision. It should not be used as a pressure control since dangerous pressures may develop if the system becomes clogged or is closed. A Model 31B manual needle valve is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Dichlorodifluoromethane is classified by the DOT as a nonflammable compressed gas and is shipped with the required "Green Label".

Commercial Preparation

Dichlorodifluoromethane is obtained by fluorination of carbon tetrachloride with hydrogen fluoride in the presence of a catalyst (partially fluorinated antimony pentachloride).

Chemical Properties

Dichlorodifluoromethane is thermally stable. It is nonflammable in any mixture with air and will not explode or propagate a flame. It is hydrolytically stable; its hydrolysis rate in water in the presence of steel being only 0.010 kg/l/year. It is noncorrosive under normal conditions to all common metals of construction, but it is corrosive at elevated temperatures. Dichlorodifluoromethane undergoes disproportionation in the presence of aluminum halides at 100–175 °C into chlorotrifluoromethane and carbon tetrachloride. Dichlorodifluoromethane does not react with most metals below temperatures of 200 °C or with acids or oxidizing agents. Dichlorodifluoromethane reacts very slowly with alkali in the presence of water but can be decomposed with molten alkali metals. It reacts vigorously with molten aluminum.

Thermodynamic and Detailed Physical Data

Molecular Structure

CCl_2F_2 has point group C_{2v} symmetry and a symmetry number of two. The C—Cl and C—F bond distances are 1.77 Å (1.77×10^{-10} m) and 1.33 Å (1.33×10^{-10} m), respectively. The F-C-F and Cl-C-Cl bond angles are 109.5 ± 3° and 108.5 ± 2 °, respectively (1). Gaseous CCl_2F_2 has a dipole moment of 1.7×10^{-30} C·m (0.51 D).

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous dichlorodifluoromethane.

Vapor Pressure (3)

Temperature °K	Temperature °F	Vapor Pressure kPa	Vapor Pressure bar	Vapor Pressure atm	Vapor Pressure mmHg
172.04	−150	1.059	0.010 6	0.010 5	7.94
199.82	−100	9.846	0.098 5	0.097 2	73.85
227.59	−50	49.07	0.490	0.484	368.0
255.37	0	164.50	1.645	1.623	1 233.3
283.15	50	423.30	4.233	4.178	3 175.0
310.93	100	909.20	9.092	8.973	6 819.0
338.71	150	1 718.9	17.19	16.965	12 893.0
366.48	200	2 965.4	29.65	29.266	22 242.0
385.15	233.6 (C.T.)	4 115.5	41.16	40.62	30 869.0 (C.P.)

The vapor pressure of liquid CCl_2F_2 between 203.15 °K and 384.65 °K is represented by the following equation (4):

$$\log_{10} P = 31.631\,5 - \frac{181\,6.5}{T} - 10.859 \log_{10} T + 0.007\,175T$$

in which P = atm and T = °K.

See Table 1 and Figure 3 for additional vapor pressure data.

Latent Heat of Vaporization, ΔHv @ -29.8 °C ..... 165 133.0 J/kg; 39.47 kcal/kg

Thermodynamic Data

See Tables 1 and 2 for the thermodynamic properties of saturated and superheated dichlorodifluoromethane, respectively.

Matheson

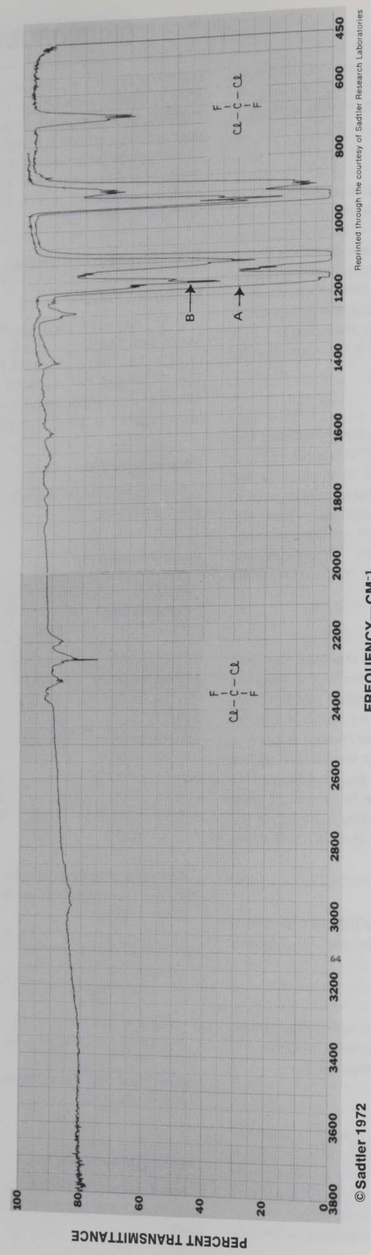


Fig. 2. Infrared spectrum of gaseous CCl_2F_2 in the frequency range 3 800–450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure: curve A (complete scan) 2.666 kPa (20 mmHg), curve B (partial scan): 0.067 kPa (0.5 mmHg) (6).

Matheson

Thermodynamic Properties of Dichlorodifluoromethane as Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	72.412 J/(mol·°K)	Enthalphy Difference, $H_{298}^\circ - H_0^\circ$	14.866 kJ/mol
Entropy, S°	300.876 J/(mol·°K)	Enthalpy of Formation, ΔH_f°	-491.620 kJ/mol
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	-300.876 J/(mol·°K)	Free Energy of Formation, ΔF_f°	-452.717 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of dichlorodifluoromethane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 119–123, Matheson, Lyndhurst, New Jersey.

[3] *Thermodynamic Properties of Freon-12 Refrigerant*, Tech. Bull. T-12, *1956*, E. I. duPont de Nemours & Co., Inc., Wilmington, Delaware.

[4] W. K. Gilkey, F. W. Gerard, and M. E. Bixler, *Ind. Eng. Chem.* 23, 364 (1931).

[5] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[6] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Matheson

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED CCl_2F_2 LIQUID AND VAPOR (3)

Temperature		Pressure			Entropy J/(KG·°K)		Enthalpy kJ/KG		Latent Heat of Vaporization kJ/KG	Specific Volume M^3/KG		Density KG/M^3	
°K	°F	kPa	bar	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
172.04	−150	1.059	0.010 6	0.010 45	−261.998	866.548	−52.758	141.412	194.170	0.000 597	11.153	1 675.0	0.089 66
177.59	−140	1.767	0.017 7	0.017 44	−234.819	845.503	−48.004	143.874	191.878	0.000 603	6.896	1 658.4	0.145 01
188.71	−120	4.430	0.044 3	0.043 68	−182.937	809.981	−38.504	148.885	187.389	0.000 613	2.918	1 613.3	0.454 96
199.82	−100	9.846	0.098 5	0.097 17	−133.909	781.697	−28.977	153.990	182.967	0.000 623	1.384	1 605.1	0.722 54
210.93	−80	19.862	0.199	0.196 0	−87.287	759.103	−19.398	159.148	178.546	0.000 635	0.720 0	1 574.8	1.388 9
222.04	−60	36.937	0.369	0.364 6	−42.735	741.154	−9.744	164.322	174.066	0.000 647	0.404 4	1 545.6	2.472 8
233.15	−40	64.174	0.642	0.633 3	0.000	726.886	0.000	169.482	169.482	0.000 659	0.241 9	1 517.5	4.133 9
244.26	−20	105.262	1.053	1.039	41.133	715.548	9.846	174.589	164.743	0.000 673	0.152 5	1 485.9	6.557 4
255.37	0	164.433	1.645	1.623	80.847	706.594	19.806	179.612	159.806	0.000 689	0.100 4	1 451.4	9.960 2
266.48	20	246.391	2.464	2.432	119.307	699.523	29.899	184.526	154.627	0.000 705	0.068 6	1 418.4	14.577
277.59	40	356.259	3.563	3.516	156.703	693.958	40.150	189.293	149.143	0.000 723	0.048 3	1.383.1	20.704
288.71	60	499.408	4.994	4.929	193.217	689.481	50.594	193.880	143.286	0.000 744	0.034 9	1 344.1	28.653
299.82	80	681.685	6.817	6.728	229.078	685.841	61.284	198.233	136.949	0.000 766	0.025 7	1 305.5	38.911
310.93	100	909.189	9.092	8.973	264.542	682.620	72.290	202.294	130.004	0.000 792	0.019 2	1 262.6	52.083
322.04	120	1 188.31	11.88	11.728	299.909	679.523	83.710	205.969	122.259	0.000 822	0.014 6	1 216.5	68.493
333.15	140	1 525.95	15.26	15.060	335.578	676.093	95.679	209.123	113.444	0.000 858	0.011 1	1 165.5	90.090
344.26	160	1 929.29	19.29	19.041	372.071	671.658	108.396	211.538	103.142	0.000 902	0.008 49	1 108.6	117.786
355.37	180	2 406.27	24.06	23.748	410.195	665.256	122.177	212.828	90.651	0.000 959	0.006 45	1 042.8	115.039
366.48	200	2 965.37	29.65	29.266	451.418	654.838	137.614	212.171	74.557	0.001 04	0.004 79	961.54	208.768
377.59	220	3 615.82	36.16	35.685	499.695	633.834	156.310	206.959	50.649	0.001 18	0.003 32	847.46	301.205
385.15	233.6	4 115.48	41.16	40.617	568.606	568.606	183.306	183.306	0.000	0.001 79	0.001 79	558.66	558.66

Matheson®

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED CCL_2F_2 VAPOR (3)

H, ENTHALPY, kJ/KG; **S**, ENTROPY, J/(KG·°K); **V**, SPECIFIC VOLUME, M^3/KG

Pressure				Temperature, °K															
kPa	bar	atm		199.82	222.04	233.15	255.37	277.59	299.82	322.04	344.26	366.48	388.71	410.93	433.15	455.37	477.59	499.82	522.04	533.15	538.71
6.894 76	0.069	0.068	H	154.118	165.321	171.156	183.271	195.944	209.133	222.805	236.921										
			S	806.633	859.770	885.418	934.998	982.571	1 028.260	1 072.276	1 114.618										
			V	1.980 8	2.205 4	2.317 3	2.540 5	2.763 3	2.985 7	3.207 9	3.430 0										
68.948	0.689	0.680	H				181.878	194.853	208.261	222.091	236.324	250.940	265.912								
			S				772.827	821.528	868.013	912.489	955.207	996.336	1 036.000								
			V				0.248 5	0.271 9	0.295 0	0.317 8	0.340 4	0.363 0	0.385 5								
101.325	1.013	1.000	H				181.130	194.270	207.796	221.712	236.010	250.673	265.682								
			S				744.250	793.579	840.440	885.209	928.137	969.391	1 009.139								
			V				0.167 1	0.183 4	0.199 4	0.215 2	0.230 7	0.246 2	0.261 6								
137.895	1.379	1.361	H				180.261	193.601	207.266	221.282	235.652	250.371	265.419	280.784							
			S				270.568	770.651	817.972	863.076	906.213	947.634	987.508	1 025.917							
			V				0.121 0	0.133 4	0.145 4	0.157 2	0.168 8	0.180 3	0.191 7	0.203 0							
275.790	2.758	2.722	H					190.948	205.195	219.613	234.276	249.208	264.422	279.912	295.669						
			S					715.966	765.337	811.738	855.754	897.761	938.053	976.838	1 014.160						
			V					0.064 04	0.070 58	0.076 84	0.082 92	0.088 87	0.094 74	0.100 5	0.106 3						
413.685	4.137	4.083	H						202.994	217.872	232.854	248.018	263.404	279.024	294.886						
			S						732.074	779.939	824.917	867.594	908.346	947.425	985.039						
			V						0.045 55	0.050 01	0.054 27	0.058 39	0.062 42	0.066 39	0.070 31						
551.581	5.516	5.444	H						200.637	216.045	231.380	246.800	262.365	278.124	294.091						
			S						706.468	756.049	802.073	845.461	886.715	926.128	963.952						
			V						0.032 96	0.036 56	0.039 92	0.043 13	0.046 25	0.049 30	0.052 30						
689.476	6.895	6.805	H							214.118	229.850	245.538	261.302	277.209	293.289	309.556					
			S							736.258	783.496	827.679	869.435	909.225	947.299	1 294.433					
			V							0.028 44	0.031 29	0.033 97	0.036 54	0.039 05	0.041 50	0.043 91					
965.266	9.653	9.526	H							209.890	226.594	242.907	259.106	275.328	291.648	308.100					
			S							703.247	753.413	799.311	842.239	882.824	921.484	958.554					
			V							0.019 07	0.021 37	0.023 46	0.025 43	0.027 31	0.029 14	0.030 93					
1 241.06	12.41	12.25	H								223.007	240.094	256.800	273.378	289.960	306.615	323.381				
			S								728.309	776.383	820.650	862.113	901.443	938.931	974.872				
			V								0.015 79	0.017 59	0.019 23	0.020 78	0.022 27	0.023 71	0.025 12				
1 516.85	15.17	14.97	H								218.970	237.061	254.369	271.351	288.222	305.095	322.028				
			S								705.464	756.425	802.282	844.750	884.749	922.698	959.015				
			V								0.012 17	0.013 81	0.015 27	0.016 62	0.017 89	0.019 11	0.020 30				
1 792.64	17.93	17.69	H								214.256	233.746	251.791	269.238	286.430	303.538	320.655	337.830			
			S								683.122	738.016	785.839	829.478	870.230	908.765	945.458	980.604			
			V								0.009 56	0.011 16	0.012 51	0.013 72	0.014 85	0.015 93	0.016 97	0.017 98			
2 068.43	20.68	20.41	H									230.062	249.041	267.030	284.582	301.945	319.253	336.579			
			S									720.359	770.651	815.671	857.260	896.338	933.450	968.931			
			V									0.009 18	0.010 46	0.011 59	0.012 62	0.013 59	0.014 52	0.015 42			
2 344.22	23.44	23.14	H									225.857	246.080	264.712	282.669	300.314	317.828	335.313			
			S									702.577	756.216	802.826	845.377	885.125	922.656	958.429			
			V									0.007 60	0.008 88	0.009 95	0.010 91	0.011 80	0.012 65	0.013 47			
2 620.01	26.20	25.86	H									220.841	242.858	262.274	280.688	298.640	316.378	334.030			
			S									683.707	742.074	790.650	834.331	874.749	912.781	948.889			
			V									0.006 28	0.007 61	0.008 64	0.009 55	0.010 38	0.011 17	0.011 92			
2 895.80	28.96	28.58	H									214.293	239.299	259.692	278.636	296.924	314.899	332.730	350.515		
			S									661.574	727.932	778.977	823.871	865.042	903.577	940.061	983.366		
			V									0.005 09	0.006 55	0.007 58	0.008 45	0.009 24	0.009 97	0.010 67	0.011 34		
3 171.59	31.72	31.30	H										235.287	256.946	276.500	295.165	313.395	331.412	349.343		
			S										713.288	767.513	813.872	855.879	894.958	931.860	966.964		
			V										0.005 64	0.006 69	0.007 53	0.008 29	0.008 98	0.009 64	0.010 27		
3 447.38	34.47	34.02	H										230.627	254.008	274.277	293.356	311.861	330.080	348.160	357.179	361.686
			S										697.556	756.132	804.207	847.134	886.841	924.120	959.517	976.587	984.997
			V										0.004 85	0.005 93	0.006 76	0.007 49	0.008 15	0.008 77	0.009 36	0.009 65	0.009 80
3 792.12	37.92	37.43	H										223.242	250.006	271.365	291.027	309.909	328.390	346.670	355.768	360.314
			S										674.712	741.781	792.408	836.716	877.176	914.999	950.772	968.052	976.504
			V										0.003 92	0.005 12	0.005 95	0.006 65	0.007 28	0.007 86	0.008 42	0.008 69	0.008 82
4 136.85	41.37	40.83	H										211.580	245.547	268.287	288.619	307.910	326.675	345.164	345.348	358.931
			S										641.616	726.928	780.860	826.633	868.013	906.422	942.613	960.019	968.596
			V										0.002 96	0.004 42	0.005 27	0.005 95	0.006 55	0.007 11	0.007 64	0.007 89	0.008 01

Matheson®

DICHLORODIFLUOROMETHANE

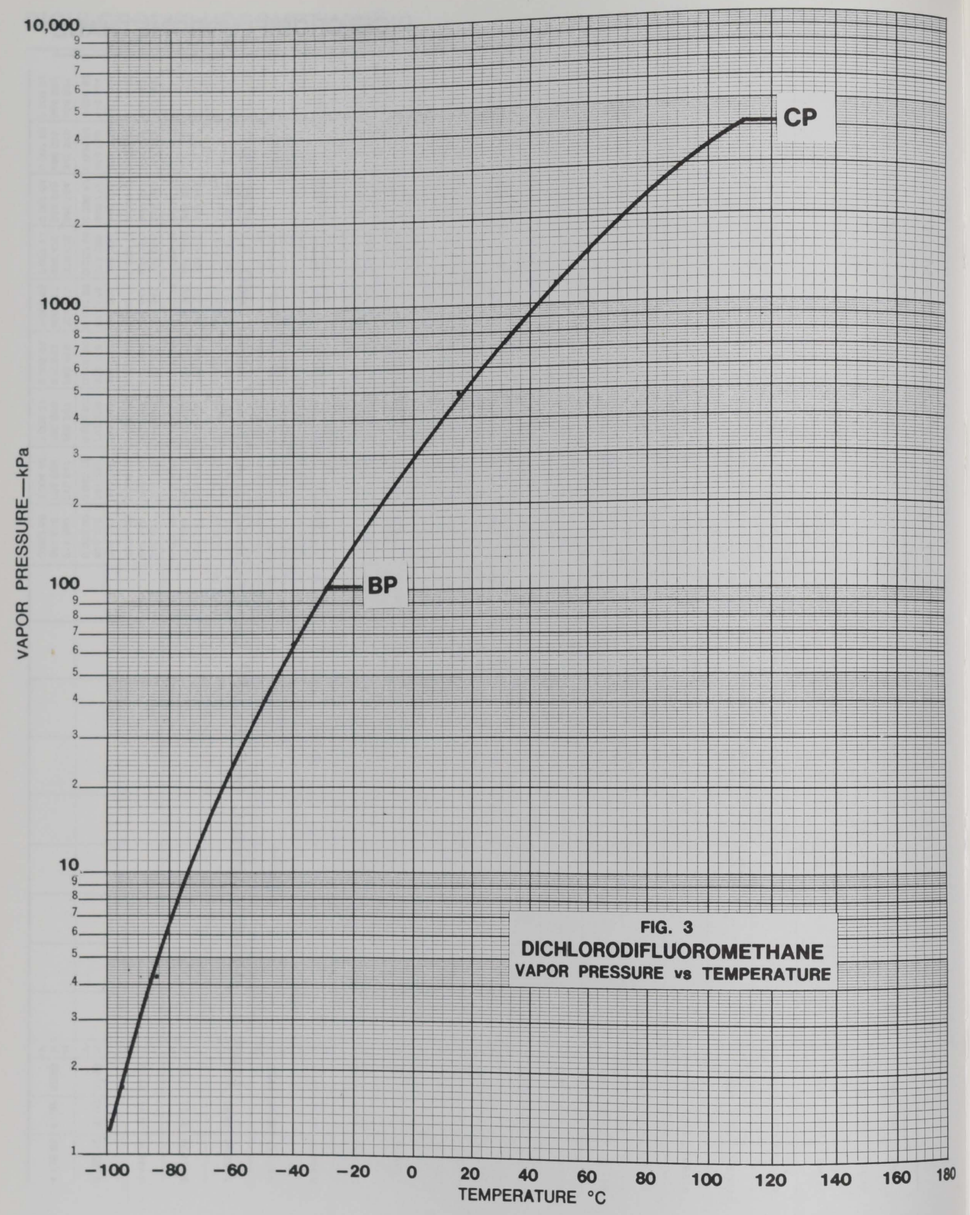


FIG. 3
DICHLORODIFLUOROMETHANE
VAPOR PRESSURE vs TEMPERATURE

Matheson

DICHLOROFLUOROMETHANE

(Synonym: Freon-21®)
(Formula: $CHCl_2F$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.102 923 kg
One Mole of $CHCl_2F$	0.102 923 kg
Specific Volume @ 21.1 °C, 101.325 kPa	218.5 dm^3/kg; 3.5 ft^3/lb
Vapor Pressure @ 21.1 °C	159.2 kPa; 1.59 bar; 23.1 psia; 1.57 atm
Boiling Point @ 101.325 kPa	282.07 °K; 8.9 °C; 48.1 °F
Freezing Point	138.15 °K; −135.0 °C; −211.0 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	4.232 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	3.572
Density, Liquid @ −40 °C	1.514 kg/l
Critical Temperature	451.65 °K; 178.5 °C; 353.3 °F
Critical Pressure	5167.6 kPa; 51.68 bar; 749.5 psia; 51.0 atm
Critical Volume	1.914 dm^3/kg
Critical Density	0.522 kg/dm^3
Critical Compressibility Factor	0.27
Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	619.650 J/(kg·°K)
@ Constant Volume	538.899 J/(kg·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.150
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.011 5 mPa·s; 0.011 5 $mN·s/m^2$; 0.011 5 cP
Viscosity, Liquid @ 0 °C	0.41 mPa·s; 0.41 $mN·s/m^2$; 0.41 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.009 62 W/(m·°K), 23.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ 0 °C	0.123 01 W/(m·°K); 294.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 0 °C	23.6 mN/m; 23.6 dyn/cm
Solubility In Water @ 101.325 kPa @ 25 °C	0.95% (by weight)
Dielectric Constant	
Gas @ 30 °C, 50.7 kPa	1.003 5
Liquid @ 28 °C	5.34
Refractive Index, Liquid, n_D @ 25 °C	1.354
Relative Dielectric Strength (Nitrogen = 1)	1.85

Description

Dichlorofluoromethane is a colorless, practically odorless, nonflammable, relatively nontoxic gas at room temperature and atmospheric pressure. Cylinders, truck cargo tanks, portable tanks, single-unit tank cars and ton multi-unit tanks are variously authorized for the shipment of $CHCl_2F$. It is readily liquefied and is reshipped in steel cylinders as a liquefied gas under its own vapor pressure of 58 kPa (8.4 psig) at 21.1 °C.

Specifications

Dichlorofluoromethane has a minimum purity of 99.0%.

Uses

Dichlorofluoromethane is used as a refrigerant, as an aerosol propellant and as a solvent.

Toxicity and Effects in Man (2)

Dichlorofluoromethane is relatively nontoxic. It is classified by the Underwriters' Laboratories as between Groups 5a and b, much less toxic than Group 4 and somewhat more toxic than Group 6. Group 4 includes those gases and vapors which in concentrations of 2–2.5% for durations of exposure of 2 hours are lethal or produce serious injury. Group 6 includes those

Matheson

gases or vapors which in concentrations somewhat lower than 20% by volume for durations of exposure of 2 hours do not appear to produce harmful effects.

Inhalation of high concentrations of gas can cause such symptoms as dizziness, disorientation, incoordination, narcosis, nausea, or vomiting. There appear to be no irreversible effects once the oxygen deficiency has been corrected.

The 1979 ACGIH has established 1 000 ppm (4200 mg/m^3) Threshold Limit Value (TLV)* for dichlorofluoromethane in air.

First Aid Treatment

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration and oxygen simultaneously. Treat symptomatically thereafter.

Precautions in Handling and Storage

The general instructions listed in Appendix I should be observed.

Leak Detection

Leaks of dichlorofluoromethane may be detected by applying soap water solution to suspected points; leaks will be indicated by bubble formation. Leaks of dichlorofluoromethane in dark, confined or inaccessible spaces or locations may be located by means of a halide torch or lamp. The Matheson Leak Detector Models 8016 and 8017 provide more sensitive leak detection.

Disposal of Leaking Cylinders

Cylinders containing dichlorofluoromethane that develop leaks which cannot be corrected normally may be disposed of according to the procedure described in Appendix II-C.

Materials of Construction

Most of the commonly used metals (steel, cast iron, brass, copper, tin, lead, aluminum) may be used satisfactorily with dichlorofluoromethane under normal conditions of use. At high temperatures, some of the metals may act as catalysts for the breakdown of the compound. The tendency of metals to promote thermal decomposition of dichlorofluoromethane is in the following approximate order: silver > brass > bronze > aluminum > 1340 steel > copper > nickel > 18-8 stainless steel > inconel (least decomposition). Magnesium alloys and aluminum containing more than 2% magnesium are not recommended for use in systems containing dichlorofluoromethane where water may be present.

In general, gasket materials should not contain natural rubber. Neoprene or Isoprene rubber, pressed fibers, including asbestos, with a number of insoluble binders, and metallic gaskets may be used.

* 1979 ACGIH Notice of Intent to Change to 10 ppm (40 mg/m^3).

Cylinder and Valve Description

Dichlorofluoromethane is packaged in DOT approved steel cylinders. Cylinders containing dichlorofluoromethane are equipped with brass valves with the approved alternate Compressed Gas Association (CGA) outlet connection No. 660. The valve outlet has a thread size of 1.030 inches, with right-hand external threads, with a flat seat and washer (see Figure 1). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet and a 9/16"-18 threads per inch male dual valve outlet.

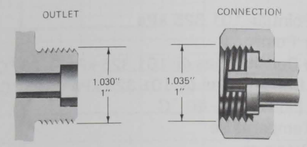


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

Safety Devices

No safety devices are required to be used in cylinders containing dichlorofluoromethane. Cylinders containing dichlorofluoromethane should not be heated in excess of 51.7 °C (125 °F) where dangerous hydrostatic pressures are built up.

Recommended Controls

Automatic Pressure Regulators

Single stage regulator Model 1P-660, having a delivery pressure range of 28–240 (4–35 psig) is recommended for use with dichlorofluoromethane.

For low pressure control, regulator Model 70-660, having a delivery pressure range of 3.4–34.5 kPa (0.5–5.0 psig), is available.

Manual Controls

Matheson needle valve Model 50-660, a brass bar stock valve, is available for direct connection to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, 1/4" compression fitting, or 1/4" NPT male or female pipe. A Model 31B manual needle valve is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Matheson

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Dichlorofluoromethane is classified as a nonflammable chemical and does not require DOT labelling.

Commercial Preparation

Dichlorofluoromethane is obtained by treating chloroform with anhydrous hydrogen fluoride in the presence of antimony chloride at elevated temperatures and pressures.

Chemical Properties

The rate of hydrolysis of dichlorofluoromethane in water alone at 30 °C (86 °F) at atmospheric pressure is less than 0.000 01 kg/l water/year; under the same conditions but in the presence of steel, the rate of hydrolysis is 0.005 2 kg/l water/year. At saturation pressure at 50 °C (122 °F) in the presence of steel, the rate of hydrolysis of dichlorofluoromethane in water is 0.009 kg/l water/year. Under neutral or acidic conditions the presence of hydrogen in the molecule has little effect on its hydrolytic stability. However, under alkaline conditions, dichlorofluoromethane tends to be hydrolyzed more rapidly. Dichlorofluoromethane in the presence of aluminum bromide or chloride is disproportionated into chlorodifluoromethane and chloroform.

Thermodynamic and Detailed Physical Data

Molecular Structure (1)

The $CHCl_2F$ molecule has C_s point group symmetry and a symmetry number of one. The C-H, C-Cl, and C-F bond distances are 1.09 Å (1.09 × 10^{-10} m), 1.75 Å (1.75 × 10^{-10} m), and 1.367 Å (1.367 × 10^{-10} m), respectively. The Cl-C-Cl, F-C-Cl, and H-C-Cl bond angles are 112.2°, 109°, and 109.75°, respectively.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous dichlorofluoromethane.

Vapor Pressure (3)

The vapor pressure of liquid $CHCl_2F$ at various temperatures is shown below.

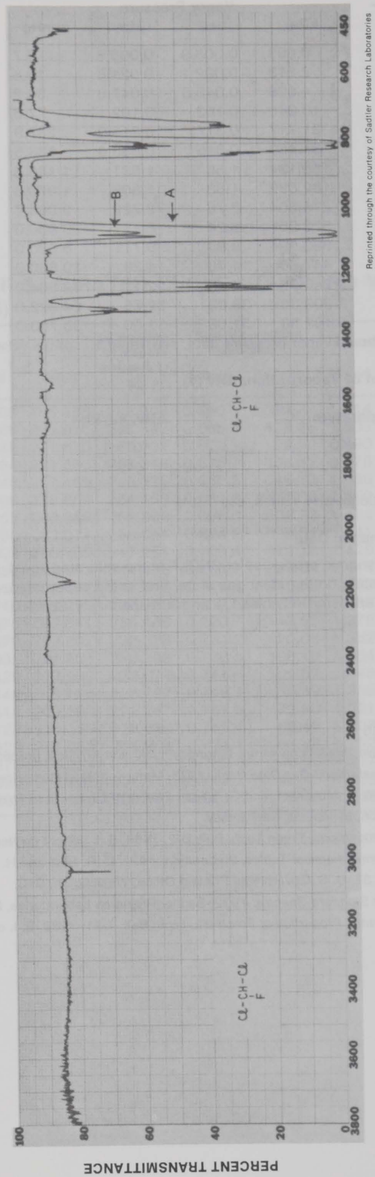


Fig. 2. Infrared spectrum of gaseous $CHCl_2F$ over the frequency range 3 800-450 cm^{-1}; 10 cm path length cell with KBr windows; cell pressure: curve A: (complete scan) 2.666 kPa (20 mmHg), curve B: (partial scan) 0.0667 kPa (0.5 mmHg) (5).

Temperature, °K	Vapor Pressure kPa	bar	atm	mmHg
199.82	0.893	0.008 9	0.008 8	6.7
210.93	2.213	0.002 1	0.021 8	16.6
222.04	4.826	0.048 3	0.047 6	36.2
233.14	10.346	0.103	0.102 1	77.6
255.37	31.717	0.317	0.313 0	237.9
277.59	84.460	0.845	0.833 6	633.5
293.15	155.134	1.55	1.531	1 163.6
298.15	182.692	1.83	1.803	1 370.3
310.93	275.804	2.76	2.722	2 068.7
333.15	523.957	5.24	5.171	3 930.0
355.37	882.594	8.83	8.711	6 620.0
377.59	1 447.88	14.48	14.29	10 860.0
399.82	2 240.35	22.40	22.11	16 804.0
422.04	3 309.33	33.09	32.66	24 822.0
451.65	5 167.58	51.68	51.00	38 760.0

For additional vapor pressure data, see Table 1.

Latent Heat of Vaporization, ΔHv (1)

Temperature, °C	ΔHv, kJ/kg
−40	266.3
0	246.7

For additional ΔHv values, see Table 1.

Thermodynamic Data

Thermodynamic properties of $CHCl_2F$ in the saturated liquid and vapor state, in the ideal gas state, and in the superhated vapor state are listed in Tables 1, 2 and 3, respectively. Specific heat data for $CHCl_2F$ at 101.325 kPa (1 atm) are listed in Table 4.

Table 4. SPECIFIC HEAT GASEOUS $CHCl_2F$ AT 101.325 kPa (1 atm) AT CONSTANT PRESSURE (Cp) AND CONSTANT VOLUME (Cv) AND THE RATIO Cp/Cv calculated (8) UNIT: J/(kg•°K)

Temperature, °K	Cp	Cv	Ratio Cp/Cv
273.15	598.312	516.724	1.158
298.15	619.650	538.899	1.150
300	620.069	539.318	1.150
400	693.289	612.538	1.132
500	753.120	672.369	1.120
600	802.910	722.158	1.112
700	840.984	760.233	1.106

Thermodynamic Properties of Dichlorofluoromethane as Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	60.994 J/(mol·°K)
Entropy, S°	293.169 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−293.169 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	13.293 kJ/mol
Enthalpy of Formation, ΔH_f°	−283.257 kJ/mol
Free Energy of Formation, ΔF_f°	−252.810 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of dichlorofluoromethane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 119-123, Matheson, Lyndhurst, New Jersey.

[3] *Freon Fluorocarbons*, Freon Tech. Bull. B-2, 1964, E. I. dePont de Nemours & Co., Inc., Wilmington, Delaware.

[4] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDA-NBS 37, U. S. Government Printing Office, Washington, D. C.

[5] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[6] *Thermodynamic Properties of Freon-21*, Tech. Bull. T-21, *1939*, E. I. duPont de Nemours & Co., Inc., Wilmington, Delaware.

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED $CHCl_2F$ LIQUID AND VAPOR (6)

Temperature °K	Temperature °F	Pressure kPa	Pressure atm	Entropy J/(kg•°K) Liquid	Entropy J/(kg•°K) Vapor	Enthalpy kJ/kg Liquid	Enthalpy kJ/kg Vapor	Latent Heat of Vaporization kJ/kg	Specific Volume dm^3/kg Liquid	Specific Volume dm^3/kg Vapor	Density kg/dm^3 Liquid	Density kg/dm^3 Vapor
233.15	−40	9.363	0.092 4	0.000	1 142.232	0.000	266.288	266.288	0.660 5	2 003.3	1.514	0.000 50
238.71	−30	13.017	0.128 5	23.012	1 127.588	5.486	269.078	263.592	0.665 5	1 473.9	1.503	0.000 68
244.26	−20	17.775	0.175 4	45.606	1 114.199	10.948	271.870	260.922	0.671 1	1 102.5	1.490	0.000 91
249.82	−10	23.877	0.235 6	67.781	1 101.647	16.434	274.680	258.246	0.676 7	838.41	1.478	0.001 19
255.37	0	31.592	0.311 8	89.538	1 090.350	21.943	277.469	255.526	0.682 3	646.13	1.466	0.001 55
258.15	5	36.149	0.356 8	100.416	1 084.911	24.709	278.864	254.155	0.684 8	570.09	1.460	0.001 75
260.93	10	41.217	0.406 8	110.876	1 079.890	27.452	280.258	252.806	0.688 0	504.73	1.454	0.001 98
266.48	20	53.083	0.523 9	132.214	1 070.686	33.030	283.071	250.041	0.694 2	399.04	1.441	0.002 51
272.04	30	67.520	0.666 4	152.716	1 061.899	38.609	285.860	247.251	0.700 4	319.13	1.428	0.003 13
277.59	40	84.943	0.838 3	173.218	1 053.950	44.257	288.673	244.416	0.706 7	257.83	1.415	0.003 88
283.15	50	105.70	1.043	193.719	1 046.837	49.952	291.462	241.510	0.712 9	210.38	1.403	0.004 75
288.71	60	130.31	1.286	213.802	1 040.142	55.740	294.275	238.535	0.719 8	173.11	1.389	0.005 78
294.26	70	159.13	1.570	233.886	1 033.866	61.575	297.041	235.466	0.726 7	143.58	1.376	0.006 97
299.82	80	192.78	1.903	253.550	1 028.427	67.479	299.807	232.328	0.734 2	120.05	1.362	0.008 33
303.15	86	215.32	2.125	265.266	1 025.080	71.035	301.434	230.399	0.738 5	108.19	1.354	0.009 24
305.37	90	231.53	2.285	272.797	1 023.406	73.429	302.503	229.074	0.741 6	101.07	1.348	0.009 89
310.93	100	276.07	2.725	292.462	1 018.386	79.449	305.176	225.727	0.749 1	85.59	1.335	0.001 68
316.48	110	326.81	3.225	311.708	1 014.202	85.516	307.803	222.287	0.757 3	72.98	1.321	0.013 70
322.04	120	384.38	3.794	330.954	1 010.018	91.723	310.383	218.660	0.765 4	62.49	1.307	0.016 00
327.59	130	449.19	4.433	350.201	1 006.252	97.929	312.893	214.964	0.774 1	53.83	1.292	0.018 58
333.15	140	522.07	5.152	369.029	1 002.486	104.275	315.334	211.059	0.782 8	46.55	1.277	0.021 48
338.71	150	603.36	5.955	387.857	999.139	110.690	317.705	207.015	0.792 2	40.43	1.262	0.024 74
344.26	160	693.61	6.845	406.685	996.210	117.222	320.053	202.831	0.801 6	35.25	1.248	0.028 37

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED $CHCl_2F$ VAPOR (6)

H, ENTHALPY, kJ/kg; S, ENTROPY, J/(kg·°K); V, SPECIFIC VOLUME, dm^3/kg

Pressure kPa	Pressure atm		Temperature, °K 233.15	244.26	255.37	266.48	277.59	299.82	322.04	344.26	366.48	388.71	410.93	433.15	455.37	477.59
8.274	0.082	H	266.312	272.030	277.864	283.768	289.835	302.387	315.450	329.025	343.111	357.732				
		S	1 152.274	1 176.541	1 199.553	1 222.146	1 244.740	1 288.254	1 330.094	1 370.678	1 410.426	1 449.338				
		V	2 268.6	2 377.3	2 486.5	2 595.1	2 704.4	2 921.6	3 139.5	3 356.8	3 574.0	3 791.2				
48.263	0.476	H				283.141	289.231	301.852	314.962	328.537	342.693	357.360	372.492			
		S				1 078.635	1 100.810	1 144.324	1 186.582	1 227.586	1 267.334	1 306.245	1 343.901			
		V				439.6	458.5	496.4	534.1	571.8	609.5	646.8	684.8			
96.527	0.953	H						301.201	314.335	328.002	342.158	356.849	372.051	387.787		
		S						1 087.003	1 129.262	1 170.683	1 210.431	1 249.342	1 287.417	1 324.654		
		V						245.4	264.6	283.7	302.8	321.8	340.7	359.6		
137.895	1.361	H						300.620	313.800	327.514	341.717	356.477	371.679	387.415		
		S						1 057.297	1 099.555	1 140.977	1 180.725	1 219.636	1 258.129	1 295.366		
		V						170.1	183.7	197.3	210.8	224.2	237.5	250.9		
206.843	2.041	H							312.893	326.654	340.949	355.756	371.004	386.811		
		S							1 065.246	1 106.668	1 146.834	1 185.746	1 224.238	1 261.476		
		V							120.8	130.0	139.2	148.3	157.3	166.3		
275.790	2.722	H							311.940	325.817	340.182	355.059	370.354	386.206		
		S							1 040.142	1 081.564	1 122.149	1 161.478	1 199.971	1 237.209		
		V							89.27	96.33	103.4	110.3	117.2	124.0		
344.738	3.402	H							310.964	324.934	339.369	354.292	369.703	385.602		
		S							1 020.059	1 061.899	1 102.902	1 142.232	1 180.725	1 218.381		
		V							70.36	76.16	81.84	87.46	93.08	98.64		
413.685	4.083	H								324.027	338.555	353.571	369.029	384.974	401.362	418.307
		S								1 045.582	1 086.585	1 126.333	1 164.826	1 202.900	1 239.719	1 276.120
		V								62.62	67.48	72.29	77.04	81.72	86.34	90.96
482.633	4.763	H								323.121	337.742	352.827	368.308	384.347	400.781	417.772
		S								1 031.356	1 072.778	1 112.526	1 151.437	1 189.093	1 226.330	1 262.731
		V								52.98	57.23	61.41	65.55	69.61	73.60	77.60
551.581	5.444	H								322.121	336.882	352.060	367.634	383.696	400.200	417.238
		S								1 018.804	1 060.226	1 100.392	1 139.303	1 177.378	1 214.615	1 251.016
		V								45.70	49.52	53.25	56.92	60.52	64.11	67.61
620.528	6.124	H								321.168	335.998	351.270	366.913	383.045	399.595	416.680
		S								1 007.089	1 048.929	1 089.514	1 128.843	1 166.918	1 204.155	1 240.974
		V								40.04	43.52	46.90	50.21	53.46	56.67	59.84
689.476	6.805	H								320.122	335.092	350.433	366.193	382.394	399.014	416.122
		S								996.629	1 038.887	1 079.472	1 118.802	1 157.294	1 194.950	1 231.351
		V								35.49	38.71	41.81	44.84	47.82	50.74	53.63
758.423	7.485	H									334.139	349.620	365.449	381.720	398.386	415.564
		S									1 029.264	1 070.267	1 110.015	1 148.508	1 186.164	1 222.983
		V									34.75	37.64	40.45	43.19	45.88	48.54

Table 3. THERMODYNAMIC PROPERTIES OF $CHCl_2F$ AS IDEAL GAS (1)

Temperature, °K	Heat Capacity C°_p	Entropy S°	Free Energy Function $-(F^\circ_T-H^\circ_{298})/T$	Enthalpy Difference $H^\circ-H^\circ_{298}$	Enthalpy of Formation ΔH°_f	Free Energy of Formation ΔF°_f
	J/(mol·°K)			kJ/mol		
0	0.000	0.000	infinite	−13.293	−277.667	−277.667
100	37.673	241.070	339.758	−9.870	−280.257	−271.768
200	50.179	271.065	298.411	−5.468	−281.947	−262.596
298.15	60.994	293.169	293.169	0.000	−283.257	−252.810
300	61.183	293.545	293.169	0.113	−283.278	−252.622
400	70.228	312.436	295.683	6.703	−284.257	−242.245
500	77.182	328.892	300.717	14.088	−284.922	−231.660
600	82.429	343.452	306.650	22.079	−285.353	−220.965
700	86.446	356.473	312.854	30.535	−285.600	−210.208
800	89.592	368.230	319.051	39.342	−285.709	−199.435
900	92.119	378.932	325.118	48.430	−285.704	−188.648
1 000	94.182	388.748	330.996	57.748	−285.596	−177.874
1 500	100.437	428.291	357.213	106.617	−284.232	−124.256
2 000	103.357	457.633	378.807	157.649	−282.320	−71.216
2 500	104.914	480.880	396.978	209.756	−280.399	−18.673
3 000	105.822	500.097	412.609	262.458	−278.792	33.510
3 500	106.395	516.456	426.304	315.520	−277.680	85.462
4 000	106.776	530.686	438.483	368.820	−277.140	137.319
4 500	107.043	543.280	449.441	422.279	−277.190	189.092
5 000	107.236	554.568	459.399	475.851	−277.767	240.952

DICHLOROSILANE

(Formula: SiH_2Cl_2)

PHYSICAL PROPERTIES (1)

Molar Mass	0.101 010 kg
Molecular Weight	0.101 010 kg
One Mole of SiH_2Cl_2	239.1 dm^3/kg; 3.83 ft^3/lb
Specific Volume @ 21.1 °C, 101.325 kPa	167.2 kPa; 1.67 bar; 24.2 psia; 1.65 atm
Vapor Pressure @ 20 °C	281.35 °K; 8.2 °C; 46.8 °F
Boiling Point @ 101.325 kPa	151.15 °K; −122.0 °C; −187.6 °F
Melting Point	4.168 kg/m^3
Absolute Density, Gas @ 101.325 kPa @ 25 °C	3.52
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.22 kg/l
Relative Density, Liquid (H_2O = 1) @ 25 °C	449.15 °K; 176.0 °C; 348.8 °F
Critical Temperature	4 676 kPa; 46.76 bar; 678.2 psia; 46.15 atm
Critical Pressure	2.158 dm^3/kg
Critical Volume	0.463 kg/dm^3
Critical Density	0.273
Critical Compressibility Factor	4.1 – 98.8% (by volume)
Flammable Limits In Air	3.9×10^{-30} C·m; 1.17 D
Dipole Moment, Gas	0.016 3 mPa·s; 0.016 3 $mN \cdot s/m^2$; 0.016 3 cP
Viscosity, Gas @ 101.325 kPa @ 20 °C	373.15 °K; 100.0 °C; 212 °F
Autoignition Temperature	

Description

Dichlorosilane is a colorless, flammable, toxic gas at room temperature and atmospheric pressure. It has an irritating odor and it fumes in moist air, being hydrolyzed to hydrochloric acid and a mixture of polymeric siloxanes. It is shipped as a liquefied gas in low pressure steel cylinders at a pressure of 66 kPa (9.6 psig) at 20 °C.

Uses

Dichlorosilane is used chiefly for the deposition of epitaxial silicon.

Toxicity

Dichlorosilane is rapidly hydrolyzed by moisture to give hydrochloric acid and a mixture of polymeric siloxanes $(-SiH_2O-)_n$. Exposure to dichlorosilane should therefore be considered as similar to exposure to hydrogen chloride. Dichlorosilane is, consequently, considered a highly toxic gas. It is severely irritating to the upper respiratory tract and corrosive to the eyes, skin and mucous membranes. Work would probably be possible in concentrations of 10–50 ppm of dichlorosilane in air, but not for more than one hour. Work would probably be impossible in concentrations of 50–100 ppm of dichlorosilane in air. The 1979 American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a Threshold Limit Value (TLV) of 5 ppm (7 mg/m^3) for hydrogen chloride. This TLV should also be followed for dichlorosilane. However, dichlorosilane provides adequate warning for prompt voluntary withdrawal from contaminated atmospheres.

First Aid Treatment (2)

The suggestions given are those recommended for hydrogen chloride. In the event that a worker is overcome by dichlorosilane, certain first aid measures should be taken, prior to the physician's arrival. Those presented herein are based upon what is believed to be common practice in industry. Their adoption in any specific case should be subject to prior endorsement by a competent medical advisor.

(a) Remove victim as quickly as possible to fresh air.

(b) If breathing has stopped, artificial respiration should be administered. Oxygen may be given but only by experienced personnel.

(c) Keep victim comfortably warm, but not hot.

(d) Summon a physician as soon as possible.

Eye Contact

Contact of the eyes with dichlorosilane gas rapidly causes severe irritation of the eyes and eyelids. If the eyes are exposed to high concentrations of dichlorosilane, they should be immediately irrigated with copious quantities of running water for at least 15 minutes. The eyelids should be held apart during the irrigation to insure contact of water with all accessible tissues of the eyes and eyelids. Medical attention should then be obtained at once.

Skin Contact

Dichlorosilane has a corrosive action on the skin and mucous membranes. It will cause severe burns. Exposure to high concentrations may also result in dermatitis. Workers who have been exposed to a high concentration of dichlorosilane should be subjected immediately to a drenching shower of water. Their clothing should be removed as rapidly as possible while they are in the shower, and medical aid should be summoned as soon as possible. It is essential that all affected body surfaces be washed with copious quantities of running water for a sufficient time to remove all dichlorosilane.

Precautions in Handling and Storage

(a) Workers who handle dichlorosilane should wear protective clothing such as rubber or plastic aprons, rubber gloves and suitable gas-tight chemical safety goggles. Woolen outside clothing or other acid resistant fabrics are recommended for workers handling dichlorosilane.

(b) Instant-acting showers should be available in the event of an emergency.

(c) Special eye-washing fountains or similar equipment should be available for eye irrigation.

(d) Proper respiratory equipment must be provided and personnel wearing such equipment must be carefully instructed in its operation and limitations.

(e) Precautions should always be taken to prevent suckback of foreign materials into the cylinder by using a check valve, vacuum break, or trap, since such a suckback may cause the development of dangerous pressures. The cylinder valve should be closed after each use.

(f) Ground all lines and equipment used for dichlorosilane. In addition, the following general rules should be observed.

(1) Never drop cylinders or permit them to strike each other violently.

(2) Cylinders should be assigned to a definite area for storage. The area should be dry, cool, well-ventilated, and preferably fire-resistant. Keep cylinders protected from excessive temperature rise by storing them away from radiators or other sources of heat. Storage conditions should comply with local and state regulations.

(3) Cylinders may be stored in the open, but in such cases should be protected against extremes of weather and from the dampness of the ground to prevent rusting. During the summer, cylinders stored in the open should be shaded against the direct rays of the sun in those localities where extreme temperatures prevail.

(4) The valve protection cap should be left in place until the cylinder has been secured against a wall or bench, or placed in a cylinder stand, and is ready to be used.

(5) Avoid dragging, rolling or sliding cylinders, even for a short distance. They should be moved by means of a suitable hand truck.

(6) Never tamper with safety devices in valves or cylinders.

(7) When returning empty cylinders, close the valve before shipment, leaving some positive pressure in the cylinder. Mark or label the cylinder EMPTY. Do not store full and empty cylinders together.

(8) No part of a cylinder should be subjected to a temperature higher than 73.9 °C (125 °F). A flame should never be permitted to come in contact with any part of a compressed gas cylinder. Temperatures in excess of 73.9 °C (125 °F) may cause a cylinder to become liquid full and create dangerous hydrostatic pressures.

(9) Cylinder content of liquefied gases is determined by weight; the cylinder content of nonliquefied gases by gauge pressure.

(10) Before using, read all data sheets and label information associated with the use of the gas concerned.

General Precautions in Using Gases

(1) Close off main cylinder valve when not in use.

(2) Use needle valve or auxiliary cut off valve in the line. Do not rely purely on the cylinder valve.

(3) Turn over cylinders in reasonable time. Corrosive gases should be three months or less.

(4) Always use gases in areas where adequate ventilation is provided.

(5) Keep cylinders in outside storage, or have manifolds piping low pressure gas into building.

(6) Use the smallest practical size cylinder for your gas applications.

Leak Detection

Large leaks of dichlorosilane will be evident by the formation of dense white fumes on contact with the atmosphere. Small leaks of dichlorodilane may be detected by holding an open bottle of concentrated ammonium hydroxide solution near the site of the suspected leak (formation of dense white fumes). Wet blue litmus paper will turn pink when exposed to a dichlorosilane leak.

Cylinder valve leaks can usually be corrected by tightening the valve packing nut (turn clockwise as viewed from above). If valve leaks persist or leaks appear at any portion of the cylinder, advise the supplier immediately.

Disposal of Leaking Cylinders

Acid gases are corrosive and toxic, and in the case of dichlorosilane, also flammable. Therefore, put on appropriate protective equipment (face shield, rubber gloves, breathing equipment) before transporting the leaking cylinder to a safe out-of-doors area or hood with forced ventilation. Post warnings in area to prevent persons from approaching the cylinders with lit cigarettes or open flames. Then proceed as follows (3):

(1) Using the Compressed Gas Association CGA-678 fitting, attach the cylinder to a vacuum/nitrogen manifold. A vacuum steam or water ejector is ideal for scrubbing the dichlorosilane fumes. A mechanical vacuum pump can be used provided a water bubbler is installed between the cylinder and pump. A branch and valve for introducing nitrogen should be included in the line from the cylinder to the bubbler or between the cylinder and vacuum steam ejector.

(2) Evacuate the cylinder.
(3) Valve off the vacuum between the cylinder and bubbler or ejector.
(4) Fill the cylinder with nitrogen.
(5) Repeat steps 2, 3 and 4 several times to remove all the dichlorosilane.
(6) Close the cylinder valve and detach cylinder from manifold.
(7) Open the cylinder valve to vent any nitrogen remaining.
(8) Unscrew cylinder valve from cylinder body.
(9) Flush out cylinder with water.
(10) Tag cylinder and valve as defective and return to the supplier according to directions.

Materials of Construction (3)

Steel has been found to be a satisfactory construction material for handling dry dichlorosilane. To give added safety during material transfer in large-scale production, forged steel valves are preferred over cast steel valves. In the presence of moisture, however, dichlorosilane is rapidly hydrolyzed to corrosive hydrochloric acid. Hence, thorough inert gas purging must be done prior to introduction of the gas into the system.

Cylinder and Valve Description

Dichlorosilane is shipped in DOT approved low pressure steel cylinders. Matheson uses stainless steel valves with the approved alternate Compressed Gas Association (CGA) cylinder valve outlet connection No. 678 on all cylinders of dichlorosilane. This cylinder valve outlet has a thread size of 1.030 inches diameter, having left-hand external threads. See Figure 1 for an illustration of this valve outlet and its mating connection.

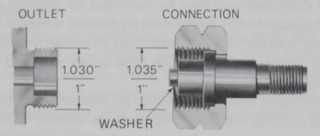


Fig. 1. CONNECTION 678 1.030"-14 LH EXT. (Short Nipple) using Flat Seat with Washer

Safety Devices

The valves on all cylinders of dichlorosilane contain a built-in fusible metal plug, melting about 72.8 °C (163 °F). The plug is protected from the cylinder contents by a frangible metal disc rated at 1 720 kPa (250 °F).

Recommended Controls

Automatic Pressure Regulator

Single stage regulator Model 3455-678, having a delivery pressure range of 0–138 kPa (0–20 psig), is recommended for use with dichlorosilane. It has a delivery pressure gauge which indicates both vacuum up to 30 inches and delivery pressure up to 210 kPa (30 psig). All metal parts of the regulator in the gas stream, including the diaphragm, are type 316 stainless steel. The seat is Kalrez and gaskets are Teflon. The inlet is a standard ¼" Gyrolok or optional ⅜" Gyrolok tube connection. It has a diaphragm packless outlet valve with ¼" Gyrolok tube fitting. The maximum inlet pressure is 2 760 kPa (400 psig).

A stainless steel check valve is recommended for use to prevent suckback into the regulator and cylinder.

It is also recommended that a stainless steel cross purge assembly Model 4774 be inserted between the regulator and the cylinder.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Stainless steel electronic mass flowmeters, such as Matheson Series No. 8160, should be used where accurate readings are required.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Dichlorosilane is classified by the DOT as a flammable liquid and is shipped with the required "Red Label".

Commercial Preparation

Dichlorosilane (as well as trichlorosilane) is produced by the reaction of a mixture of hydrogen and hydrogen chloride with silicon at high temperatures (4). It is also prepared (15% yield) by disproportionation of trichlorosilane by heating to 300–400 °C in the presence of acid catalysts of the metallic halide type, e.g., aluminum chloride, ferric chloride and boron trifluoride (5).

Chemical Properties

Hydrolysis of dichlorosilane by water gives hydrochloric acid and a mixture of polymeric siloxanes, the simplest of which is the tetramer $(SiH_2O)_4$ (6). Dichlorosilane forms a solid 1:1 adduct with trialkylamines and pyridine, e.g., $SiH_2Cl_2 \cdot N(CH_3)_3$ (7). Treatment of dichlorosilane with antimony trifluoride yields difluorosilane (8). Dichlorosilane deposits uniform layers of epitaxial silicon of excellent crystal quality at a temperature of about 1 000 °C, the deposition rate at 1 100 °C being much greater than that of trichlorosilane or silicon tetrachloride at this temperature; also dichlorosilane significantly lowers the processing time from that required with silane and greatly reduces the raw material cost (3).

Thermodynamic and Detailed Physical Data

Molecular Structure (9)

The tetrahedral SiH_2Cl_2 molecule has C_{2v} point group symmetry, with a symmetry number of two. The Si-H bond distance is 1.48 Å (1.48 × 10^{-10} m) and the Si-Cl bond distance is 2.05 Å (2.05 × 10^{-10} m); all angles are approximately 110.47°.

Infrared Spectrum (9)

Dichlorosilane has nine infrared active vibrations, the fundamental frequencies (in cm^{-1}) and assignments (in parentheses) of which are as follows: 2 200 (ν_1); 953 (ν_2); 531 (ν_3); 188 (ν_4); 710 (ν_5); 2 200 (ν_6); 610 (ν_7); 877 (ν_8); 592 (ν_9).

Vapor Pressure (3)

Vapor pressure data up to 101.325 kPa (1 atm) are shown below:

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
202.65	1.333	13.3	10
237.15	13.332	133.3	100
253.15	31.997	320.0	240
257.15	39.997	400.0	300
265.15	55.329	553.3	415
273.15	81.327	813.3	610
281.35	101.325	1 013.25	760

Vapor pressure data above 101.325 kPa are shown below.

Temperature, °K	Vapor Pressure kPa	bar	atm
281.35	101.325	1.013	1.00
293.15	167.186	1.67	1.65
313.15	303.975	3.04	3.00
333.15	526.890	5.27	5.20
373.15	1 276.695	12.8	12.60
449.15	4 676.149	46.8	46.15

See Figure 2 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv(3) @ 8.2 °C	269.64 KJ/kg; 64.44 kcal·kg

Thermodynamic Properties of Dichlorosilane As Ideal Gas @ 25 °C (9)

Heat Capacity, C_p°	62.053 J/(mol·°K)
Entropy, S°	286.596 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−286.596 J/(mol·°K)
Enthalpy Difference $H_0^\circ - H_{298}^\circ$	−13.364 kJ/mol
Enthalpy of Formation, ΔH_f°	−313.800 kJ/mol
Free Energy of Formation, ΔF_f°	−288.315 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of dichlorosilane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker and A. L. Mossman, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 1st edition, *1970*, pp. 71–73, Matheson, East Rutherford, New Jersey.

[3] *Dichlorosilane*, Tech. Bull. No. F-43495A, *1971*, Union Carbide Corporation, New York, New York.

[4] F. G. A. Stone, *Hydrogen Compounds of the Group IV Elements*, *1962*, p. 15, Prentice-Hall, Inc. Englewood Cliffs, New Jersey.

[5] C. E. Erickson and G. H. Wagner, *U. S. Patent 2, 627, 451 (1953)* and *U. S. Patent 2, 735, 861 (1956)*.

[6] C. H. Van Dyke in Kirk-Othmer's *Encyclopedia of Chemical Technology*, *1969*, Volume 18, p. 184, John Wiley & Sons, Inc., New York, New York.

[7] **Ibid.**, pp. 184–186.

[8] H. J. Emeleus and A. G. Maddock, *J. Chem. Soc. 1944*, 293.

[9] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

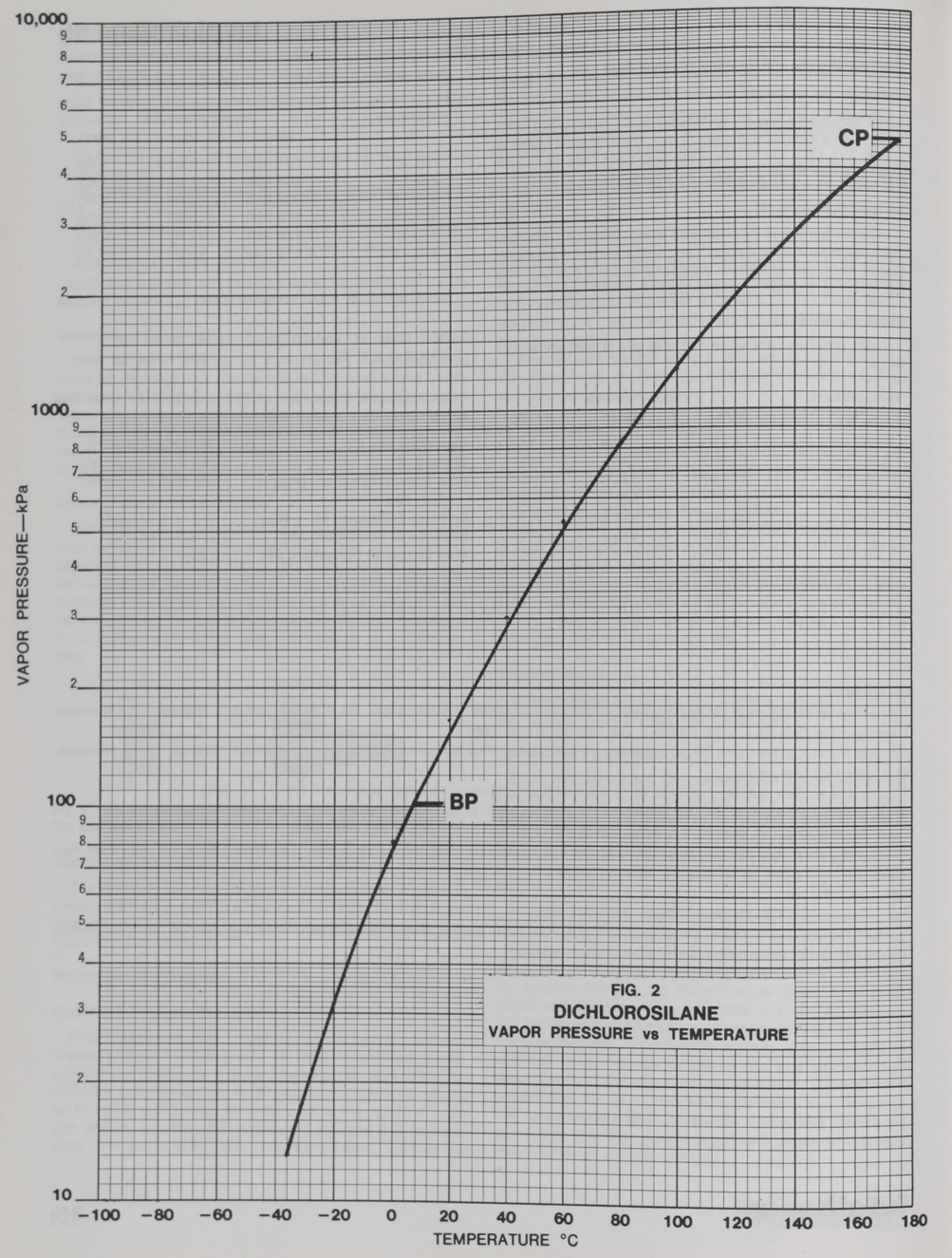


FIG. 2
DICHLOROSILANE
VAPOR PRESSURE vs TEMPERATURE

1,2-DICHLOROTETRAFLUOROETHANE

(Synonym: Freon-114®, Genetron-114®, Isotron-114®, Ucon-114®)
(Formula: $CClF_2CClF_2$ or $C_2Cl_2F_4$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.170 922 kg
One Mole of $C_2Cl_2F_4$	0.170 922 kg
Specific Volume @ 21.1 °C, 101.325 kPa	143.6 dm^3/kg; 2.3 ft^3/lb
Vapor Pressure @ 21.1 °C	190.3 kPa; 1.88 atm; 1.90 bar; 27.6 psia
Boiling Point @ 101.325 kPa	276.92 °K; 3.8 °C; 38.8 °F
Freezing Point	179.15 °K; −94.0 °C; −137.2 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	7.027 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25°C (Air = 1)	5.93
Density, Liquid @ Saturation Pressure @ 0 °C	1.529 kg/l
Critical Temperature	418.85 °K; 145.7 °C; 294.3 °F
Critical Pressure	3 262.7 kPa; 32.63 bar; 473.2 psia; 32.2 atm
Critical Volume	1.720 dm^3/kg
Critical Density	0.581 kg/dm^3
Critical Compressibility Factor	0.275
Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	661.072 J/(kg·°K);
@ Constant Volume	612.119 J/(kg·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C Cp/Cv	1.080
Specific Heat, Liquid @ 0 °C	999.98 J/(kg·K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.011 8 mPa·s; 0.011 8 $mN·s/m^2$; 0.011 8 cP
Viscosity, Liquid @ 0 °C	0.485 mPa·s; 0.485 $mN·s/m^2$; 0.485 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.011 09 W/(m·°K); 26.5 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ 0 °C	0.092 88 W/(m·°K); 222.0 × 10^{-6} cal·cm/(s·cm^2· °C)
Surface Tension @ 0 °C	26.1 mN/m; 26.1 dyn/cm
Solubility in Water @ 101.325 kPa @ 25 °C	0.013% (by weight)
Solubility of Water in $C_2Cl_2F_4$ @ 30 °C	0.011% (by weight)
Dielectric Constant	
Gas @ 26.8 °C, 50.7 kPa	1.002 1
Liquid @ 25°C	2.26
Refractive Index, Liquid, n_D @ 25 °C	1.288
Relative Dielectric Strength (Nitrogen = 1)	3.34

Description

1,2-Dichlorotetrafluoroethane is a colorless, odorless, nonflammable, relatively nontoxic gas at room temperature and atmospheric pressure. Cylinders, truck cargo tanks, portable tanks, single-unit tank cars and ton multi-unit tanks are variously authorized for shipment of $C_2Cl_2F_4$. It is readily liquefied and is reshipped in steel cylinders as a liquefied gas under its own vapor pressure of 89 kPa (12.9 psig) at 21.1 °C.

Specifications

1,2-Dichlorotetrafluoroethane has a minimum purity of 95.0 mole %.

Toxicity and Effects in Man (2)

1,2-Dichlorotetrafluoroethane has a very low degree of toxicity. It is classified by the Underwriters' Laboratories in Group 6, a category which includes those gases or vapors which in

concentrations up to at least 20% by volume for durations of exposure of the order of 2 hours do not appear to produce injury.

Inhalation of high concentrations of gas can cause such symptoms as dizziness, disorientation, incoordination, narcosis, nausea, or vomiting. There appear to be no irreversible effects once the oxygen deficiency has been corrected.

The 1979 ACGIH has established a Threshold Limit Value (TLV) of 1 000 ppm (7 000 mg/m^3) for 1,2-dichlorotetrafluoroethane in air.

First Aid Treatment

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration and oxygen simultaneously. Treat symptomatically thereafter.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Leak Detections

Leaks of 1,2-dichlorotetrafluoroethane may be detected by applying soap water solution to suspected points; leaks will be indicated by bubble formation. Leaks of 1,2-dichlorotetrafluoroethane in dark, confined, or inaccessible spaces or locations may be located by means of a halide torch or lamp. The Matheson Leak Detector Model 8016 and 8017 provides a more sensitive means of leak detection.

Disposal of Leaking Cylinders

Cylinders containing 1,2-dichlorotetrafluoroethane which develop leaks that cannot be corrected normally may be disposed of by the procedure described in Appendix II-C.

Materials of Construction

Most of the commonly used metals (steel, cast iron, brass, copper, tin, lead, aluminum) may be used satisfactorily with 1,2-dichlorotetrafluoroethane under normal conditions of use. At high temperatures some of the metals may act as catalysts for the breakdown of the compound. The tendency of metals to promote thermal decomposition of Freon-114 is in the following approximate order: silver > brass > bronze > aluminum > 1340 steel > copper > nickel > 18-8 stainless steel > inconel (least decomposition). Magnesium alloys and aluminum containing more than 2% magnesium are not recommended for use in systems containing 1,2-dichlorotetrafluoroethane where water may be present.

In general gasket materials should not contain natural rubber. Neoprene or Isoprene rubber, pressed fibers, including asbestos, with a number of insoluble binders, and metallic gaskets may be used.

Cylinder and Valve Description

1,2-dichlorotetrafluoroethane is packaged in DOT approved steel cylinders. Cylinders containing 1,2-dichlorotetrafluoroethane are equipped with brass valves with the approved alternate Compressed Gas Association (CGA) outlet connection No. 660. The valve outlet has a thread size of 1.030 inches, with right-hand external threads, usedd with a flat-seat and washer (see Figure 1). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet and a 9/16″-18 threads per inch male dual valve outlet.

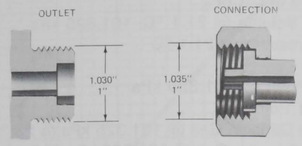


Fig. 1. CONNECTION 660 1.030″-14 RH EXT. using Flat Seat with Washer

Safety Devices

No safety devices are required to be used in cylinders containing 1,2-dichlorotetrafluoroethane. The cylinders should, therefore, not be excessively heated to the point where dangerous hydrostatic pressures are built up.

Recommended Controls

Automatic Pressure Regulators

Matheson Model 70 low pressure regulators provide satisfactory low pressure control. These regulators have oversize, pancake bodies of die cast aluminum with Buna N diaphragms. The following models are available:

Model No.	Delivery Pressure Range kPa	mbar (g)	psig
70B-660	0.5–2.99	5–29.9	2–12 inches water column
70-660	3.4–34.5	34–345	0.5–5.0 psig
70A-660	34.5–68.9	345–689	5–10 psig

Manual Controls

Matheson needle valves Model 50-660, a brass bar stock valve, is available for direct connection to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, ¼″ compression fitting, or ¼″ NPT male or female pipe. A Model 31B manual needle valve is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a poteniometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

1,2-Dichlorotetrafluoroethane is not classified by the DOT as a compressed gas, and requires no special label.

Commercial Preparations

1,2-Dichlorotetrafluoroethane is obtained by treating hexachloroethane with anhydrous hydrogen fluoride in the presence of small amounts of antimony chloride under high pressure.

Chemical Properties

1,2-Dichlorotetrafluoroethane is comparatively thermally stable. Its rate of hydrolysis in water at 30 °C and 1 atm is less than 0.000 005 kg/l water/year; under similar conditions but in the presence of steel, the rate is 0.001 4 kg/l water/year. At saturation pressure and 50 °C in the presence of steel, the rate of hydrolysis in water is 0.003 kg/l water/year.

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

The $C_2Cl_2F_4$ molecule has C_i symmetry, with C—C, C—Cl, and C—F bond distances of 1.54 Å (1.54 × 10^{-10} m), 1.75 Å (1.75 × 10^{-10} m), and 1.33 Å (1.33 × 10^{-10} m), respectively.

Infrared Spectrum

For infrared spectrum of gaseous 1,2-dichlorotetrafluoroethane, see Figure 2.

Vapor Pressure (4)

Temperature °K	Temperature °F	Pressure kPa	Pressure bar	Pressure atm	Pressure mmHg
233.15	−40	13.141	0.131	0.130	98.6
244.26	−20	23.925	0.239	0.236	179.5
255.37	0	41.017	0.410	0.405	307.7
266.48	20	66.783	0.668	0.659	500.9
273.15	32	87.529	0.875	0.864	656.5
277.59	40	103.959	1.040	1.026	779.8
288.71	60	155.642	1.556	1.536	1 167
293.15	68	181.118	1.811	1.787	1 358
298.15	77	213.469	2.134	2.107	1 601
299.82	80	225.176	2.353	2.222	1 689
310.93	100	316.131	3.161	3.120	2 371

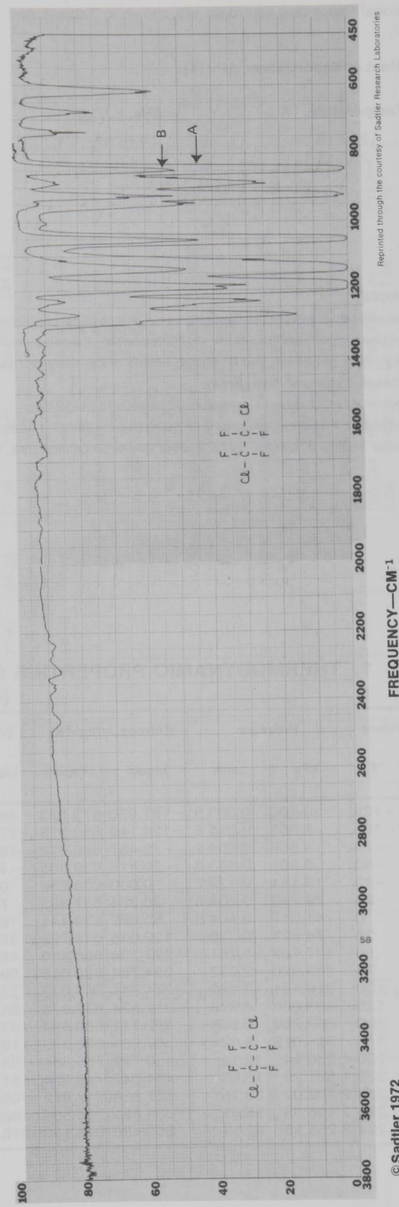


Fig. 2. Infrared spectrum of gaseous $C_2Cl_2F_4$ in the 3 800-450 cm^{-1} region; 10 cm cell path length; KBr optics; cell pressure: curve A (complete scan): 2.666 kPa (20 mmHg), curve B (partial scan): 0.066 7 kPa (0.5 mmHg) (5).

Additional vapor pressure data are shown in Table 1 and Figure 3.

Latent Heat of Vaporization, ΔHv (4)

Temperature, °K	ΔHv, kJ/kg
233.15	148.91
253.15	143.51
273.15	137.32
276.92	136.06

Thermodynamic Data

See Tables 1 and 2 for the thermodynamic properties of saturated and superheated 1,2-dichlorotetrafluoroethane, respectively.

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED $C_2Cl_2F_4$ LIQUID AND VAPOR (4)

Temperature		Pressure		Entropy J/(kg·°K)		Enthalpy kJ/kg		Latent Heat of Vaporization kJ/kg	Specific Volume dm³/kg		Density kg/dm³	
°K	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
185.93	−125	0.400	0.003 9	−181.920	679.523	−38.046	122.127	160.173	0.572 2	22 436	1.748	0.000 045
199.82	−100	1.365	0.013 5	−126.148	659.315	−27.289	129.664	156.953	0.582 8	7 107	1.716	0.000 141
213.71	−75	3.868	0.038 2	−72.467	646.679	−16.190	137.505	153.695	0.594 2	2 677	1.683	0.000 374
227.59	−50	9.501	0.093 8	−20.418	639.985	−4.709	145.608	150.317	0.606 4	1 158	1.649	0.000 864
233.15	−40	13.141	0.129 7	0.000	638.688	0.000	148.913	148.913	0.611 5	855.6	1.635	0.001 17
241.48	−25	29.719	0.204 5	30.334	637.893	7.199	153.929	146.730	0.619 5	560.2	1.614	0.001 79
255.37	0	41.017	0.404 8	80.082	639.441	19.572	162.421	142.849	0.633 8	296.8	1.578	0.003 37
269.26	25	74.891	0.739 1	129.035	643.708	32.433	171.023	138.590	0.649 3	169.3	1.540	0.005 91
283.15	50	127.787	1.261	177.234	650.110	45.787	179.680	133.893	0.666 2	102.7	1.501	0.009 74
297.04	75	205.926	2.032	224.764	658.018	59.624	188.324	128.700	0.685 1	65.44	1.460	0.015 28
310.93	100	316.131	3.120	271.541	667.013	73.920	196.894	122.974	0.706 2	43.44	1.416	0.023 02
324.82	125	465.686	4.596	317.524	676.678	88.647	205.311	116.664	0.730 1	29.48	1.370	0.033 92
338.71	150	662.269	6.536	362.711	686.594	103.782	213.489	109.707	0.757 8	20.96	1.320	0.047 70
352.59	175	914.072	9.021	407.061	696.343	119.311	221.308	101.997	0.790 6	15.03	1.265	0.066 53
366.48	200	1 230.14	12.14	450.742	705.381	135.269	228.590	93.321	0.830 8	10.90	1.204	0.091 78
380.37	225	1 621.29	16.00	494.047	712.954	151.765	235.036	83.271	0.882 7	7.91	1.133	0.126 45
394.26	250	2 102.02	20.75	537.853	717.472	169.175	240.008	70.833	0.956 2	5.65	1.046	0.177 04
408.15	275	2 695.95	26.61	585.551	714.502	188.924	241.566	52.642	1.084 9	3.79	0.922	0.264 10
418.71	294	3 253.95	32.11	650.486	675.130	216.534	226.866	10.332	1.524 9	1.94	0.655 8	0.514 57

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of 1,2-dichlorotetrafluoroethane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment, 2nd edition, 1977*, pp. 119–123, Matheson, Lyndhurst, New Jersey.

[3] J. R. Lacher, *et al., J. Amer. Chem. Soc. 71*, 1330–1334 (1949).

[4] *Thermodynamic Properties of Freon 114 Refrigerant, 1966*, E. I. duPont de Nemours & Co., Wilmington, Delaware.

[5] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Matheson

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED $C_2Cl_2F_4$ VAPOR (4)
H, ENTHALPY, kJ/kg; S, ENTROPY, J/(kg·°K); V, SPECIFIC VOLUME, dm³/kg

Pressure			Temperature, °K															
kPa	atm		227.59	255.37	283.15	310.93	338.71	366.48	394.26	422.04	449.82	477.59	505.37	533.15	560.93	588.71
6.894 76	0.068	H	145.664	163.034	181.537	201.071	221.545	242.860	264.922							
		S	655.716	727.681	796.424	862.197	925.250	985.750	1 043.741							
		V	1 598.2	1 795.6	1 992.7	2 189.5	2 386.1	2 582.6	2 779.0							
34.474	0.340	H		162.541	181.125	200.727	221.252	242.609	264.703	287.441						
		S		648.185	717.221	783.245	846.465	907.049	965.123	1 020.854						
		V		354.24	394.57	434.63	474.49	514.22	553.84	593.38						
68.948	0.680	H			180.602	200.290	220.883	242.291	264.429	287.201						
		S			682.285	748.601	811.989	872.741	930.940	986.755						
		V			194.75	215.24	235.52	255.66	275.69	295.64						
103.421	1.02	H			180.068	199.846	220.508	241.972	264.152	286.960						
		S			661.323	727.932	791.529	852.448	910.773	966.671						
		V			128.11	142.08	155.85	169.46	182.96	196.38						
137.895	1.36	H				199.393	220.127	241.647	263.873	286.718	310.090					
		S				712.954	776.801	837.846	896.296	952.278	1 005.875					
		V				105.49	116.00	126.35	136.60	146.75	156.85					
413.685	4.08	H					216.868	238.925	261.556	284.716	308.344	332.358				
		S					716.677	779.270	838.766	895.543	949.726	1 001.524				
		V					36.15	40.05	43.81	47.46	51.04	54.57				
689.476	6.80	H						235.910	259.064	282.606	306.153	330.448	354.998			
		S						748.518	809.437	867.134	921.986	974.286	1 024.160			
		V						22.67	25.18	27.56	29.86	32.09	34.28			
965.266	9.53	H						232.482	256.349	280.365	304.625	329.132	353.848			
		S						725.296	788.056	846.925	902.572	955.458	1 005.750			
		V						15.10	17.14	19.01	20.76	22.45	24.08			
1 241.06	12.25	H							253.343	277.969	302.636	327.437	352.379	377.420		
		S							770.149	830.524	887.134	940.605	991.357	1 039.598		
		V							12.61	14.22	15.69	17.08	18.42	19.71		
1 516.85	14.97	H							249.934	275.379	300.541	325.680	350.870	376.104		
		S							753.789	816.173	873.912	928.137	979.391	1 028.01		
		V							9.66	11.15	12.45	13.66	14.81	15.91		
1 792.64	17.69	H							245.908	272.553	298.326	323.858	349.324	374.765		
		S							737.597	802.910	862.071	917.133	968.973	1 017.967		
		V							7.53	8.99	10.20	11.29	12.31	13.27		
2 068.43	20.41	H							240.766	269.412	295.976	321.963	347.737	373.403		
		S							719.899	790.148	851.151	907.175	959.642	1 009.097		
		V							5.84	7.37	8.53	9.54	10.47	11.34		
2 344.22	23.14	H								265.842	293.461	319.990	346.107	372.018		
		S								777.345	840.733	897.970	951.107	1 001.022		
		V								6.09	7.25	8.21	9.07	8.97		
2 620.01	25.86	H								261.637	290.758	317.933	344.434	370.607		
		S								763.747	830.608	889.226	943.157	993.574		
		V								5.04	6.22	7.14	7.96	8.70		
2 895.80	28.58	H								256.349	287.822	315.783	342.718	369.173	395.330	
		S								748.225	820.524	880.858	935.710	986.671	1 034.494	
		V								4.10	5.37	6.28	7.06	7.76	8.42	

Matheson

Table 2—*Continued*

Pressure kPa	Pressure atm		Temperature, °K 227.59	255.37	283.15	310.93	338.71	366.48	394.26	422.04	449.82	477.59	505.37	533.15	560.93	588.71
3 171.59	31.30	H								248.660	284.605	313.533	340.954	367.718	394.091	420.157
		S								727.639	810.315	872.741	928.555	980.102	1 028.344	1 073.698
		V								3.19	4.66	5.56	6.32	6.98	7.60	8.19
3 447.38	34.02	H								225.889	281.044	311.178	339.146	366.239	392.840	419.074
		S								671.992	799.730	864.791	921.693	973.910	1 022.528	1 068.175
		V								1.76	4.04	4.96	5.69	6.33	6.92	7.47
3 723.17	36.74	H								209.042	277.057	308.712	337.293	364.742	391.580	417.988
		S								631.198	788.558	856.925	915.083	967.968	1 017.047	1 062.987
		V								1.21	3.51	4.44	5.16	5.78	6.34	6.87
3 998.96	39.47	H								206.422	272.567	306.129	335.399	363.227	390.311	416.901
		S								624.211	776.592	849.059	908.639	962.278	1 011.77	1 058.050
		V								1.15	3.03	4.00	4.70	5.30	5.84	6.34
4 136.85	40.83	H								205.625	270.119	304.797	334.434	362.462	389.677	416.354
		S								621.952	770.233	845.168	905.501	959.475	1 009.264	1 055.665
		V								1.13	2.82	3.80	4.50	5.09	5.62	6.11
4 412.64	43.55	H								204.451	264.859	302.048	332.479	360.921	388.401	415.267
		S								618.437	756.969	837.302	899.267	954.078	1 004.327	1 051.063
		V								1.10	2.43	3.43	4.13	4.70	5.21	5.68
4 688.43	46.27	H								203.598	259.341	299.202	330.489	359.368	387.120	414.176
		S								615.717	743.288	829.478	893.200	948.806	999.558	1 046.628
		V								1.09	2.10	3.12	3.80	4.36	4.86	5.31
4 964.22	48.99	H								202.931	253.966	296.281	328.474	357.904	385.837	413.089
		S								613.416	730.150	821.654	887.217	943.701	994.955	1 042.402
		V								1.07	1.84	2.84	3.52	4.06	4.54	4.98
5 240.02	51.71	H								202.389	249.078	293.319	326.440	356.237	384.556	412.005
		S								611.450	718.225	813.872	881.318	938.722	990.520	1 038.301
		V								1.06	1.63	2.59	3.26	3.80	4.26	4.69
5 515.81	54.44	H								201.936	244.878	290.356	324.397	354.668	383.278	410.925
		S								609.692	707.933	806.215	875.586	933.911	986.211	1 034.327
		V								1.05	1.48	2.38	3.04	3.56	4.01	4.42

Matheson®

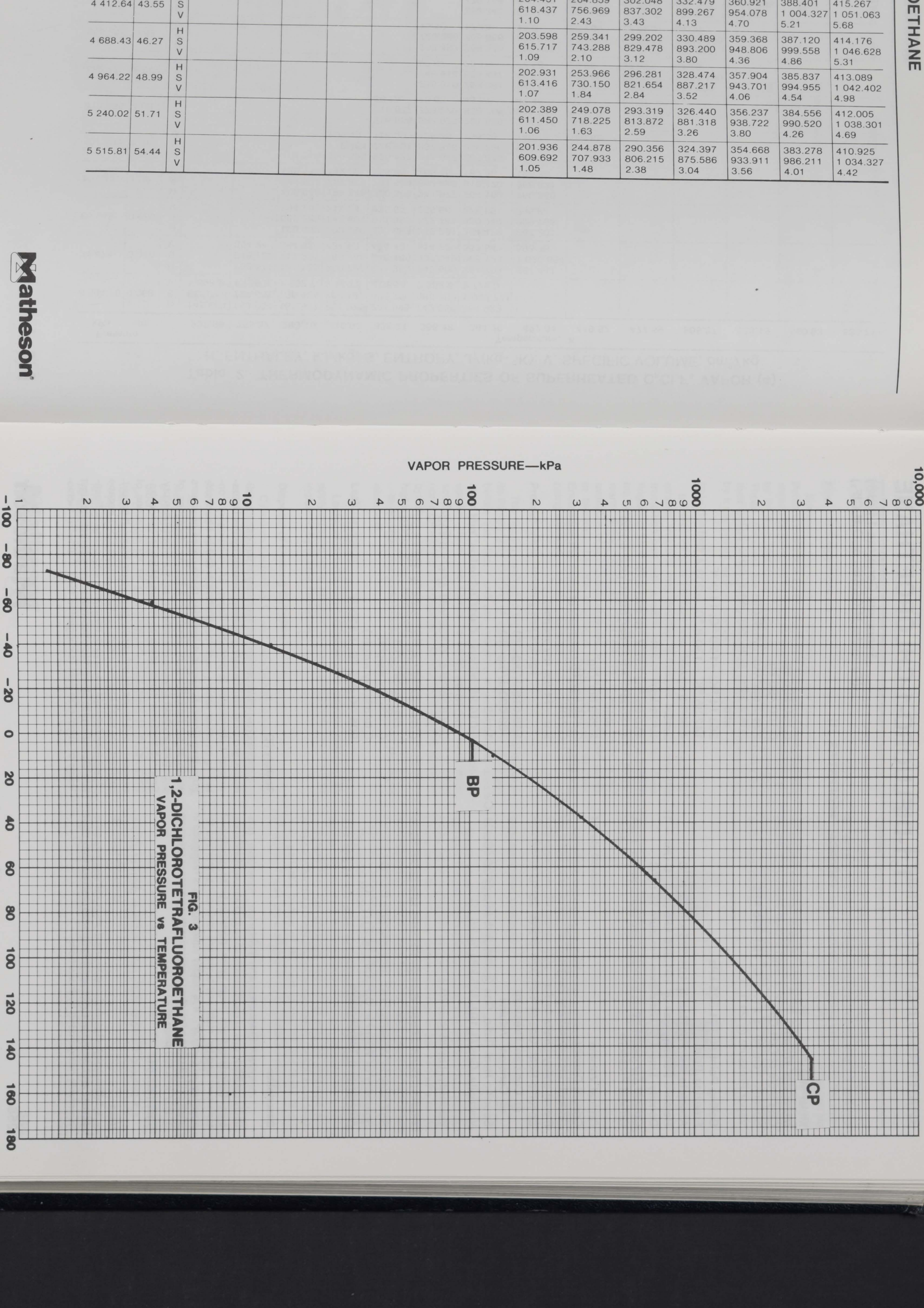


FIG. 3
1,2-DICHLOROTETRAFLUOROETHANE
VAPOR PRESSURE vs TEMPERATURE

1,1-DIFLUORO-1-CHLOROETHANE

(Synonym: Genetron-142B®)
(Formula: H_3CCClF_2 or $C_2H_3ClF_2$)

PHYSICAL PROPERTIES (1)

Molar Mass	0.100 496 kg
Molecular Weight	0.100 496 kg
One Mole of $C_2H_3ClF_2$	224.7 dm^3/kg; 3.6 ft^3/lb
Specific Volume @ 21.1 °C, 101.325 kPa	308.2 kPa; 3.08 bar; 44.7 psia; 3.04 atm
Vapor Pressure @ 21.1 °C	263.14 °K; −10.0 °C; 14.0 °F
Boiling Point @ 101.325 kPa	142.35 °K; −130.8 °C; −203.4 °F
Freezing Point	4.508 5 kg/m^3
Absolute Density, Gas @ 101.325 kPa @ 0 °C	3.49
Relative Density, Gas @ 101.325 kPa @ 0 °C (Air = 1)	1.171 kg/l
Density, Liquid @ Saturation Pressure @ 0 °C	410.25 °K; 137.2 °C; 278.8 °F
Critical Temperature	4 123 kPa; 41.23 bar; 598.0 psia; 40.69 atm
Critical Pressure	2.299 dm^3/kg
Critical Volume	0.435 kg/dm^3
Critical Density	0.279
Critical Compressibility Factor	9.0 −14.8% (by volume)
Flammability Limits In Air	
Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	848.515 J/(kg·°K)
@ Constant Volume	766.090 J/(kg·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.108
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.010 99 mPa·s; 0.010 99 mN·s/m^2; 0.010 99 cP
Viscosity, Liquid @ −20.9 °C	0.453 mPa·s; 0.453 mN·s/m^2; 0.453 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.011 84 W/(m·°K); 28.3 × 10^{-6} cal·cm/(s·cm^2·°C)
Solubility in Water @ 101.325 kPa @ 21.1 °C	0.19% (by weight)
Solubility of Water in $C_2H_3ClF_2$ @ 21.1 ° C	0.048% (by weight)
Autoignition Temperature	905 °K; 632 °C; 1 170 °F

Description

1,1-Difluoro-1-chloroethane is a colorless, flammable, relatively nontoxic gas at room temperature and atmospheric pressure. Cylinders, truck cargo tanks, portable tanks, single-unit tank cars and ton multi-unit tanks are variously authorized for shipment of $C_2H_3ClF_2$. It is readily liquefied and is reshipped in steel cylinders as a liquefied gas under its own vapor pressure of 207 kPa (30 psig) at 21.1 °C.

Specifications

1,1-Difluoro-1-chloroethane has a minimum purity of 98.0%.

Uses

1,1-Difluoro-1-chloroethane is used as a refrigerant, as a solvent and as an aerosol propellant when mixed with nonflammable halogenated hydrocarbons.

Toxicity (2)

1,1-Difluoro-1-chloroethane is relatively nontoxic. Its estimated grouping via the rating system devised by the Underwriters' Laboratories is probably Group 5A, a category containing gases or vapors much less toxic than Group 4 but more toxic than Group 6. Group 4 includes those gases or vapors which in concentrations of about 2–2.5% for durations of exposure of about 2 hours are lethal or produce serious injury. Group 6 contains those gases or vapors which in concentrations up to at least 20% by volume in air for durations of exposure of 2 hours do not appear to produce injury. It should, however, be used in adequately ventilated areas since escape of gas may produce an oxygen deficiency and cause suffocation. By analogy to other chlorofluoroalkanes, a Threshold Limit Value of about 500 ppm is suggested for 1,1-difluoro-1-chloroethane (concentration in air to which nearly all workers may be repeatedly exposed, day after day, without adverse affects).

Contact with the liquid may cause frostbite.

First Aid Suggestions (2)

Summon a physician immediately for any person overcome. Persons overcome by exposure to 1,1-difluoro-1-chloroethane should be removed to fresh air and treated for suffocation, i.e., by artificial respiration produced manually or by a pulmotor. These measures are believed to be common in industry but their adoption specifically should be subject to endorsement by a competent medical advisor.

Skin Contact

In case of skin contact with liquid 1,1-difluoro-1-chloroethane, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The hazard involved in the handling of the material is due to its flammability. Ground all equipment and cylinders of the gas before use. Store and use cylinders in well-ventilated areas away from heat and all sources of ignition such as flames and sparks. Never use flames to detect leaks, use soap water solution. Do not use the gas around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing and flammable materials.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks of 1,1-difluoro-1-chloroethane may be detected by applying soap water solution to suspected points; leaks will be indicated by bubble formation.

Disposal of Leaking Cylinders

Cylinders containing 1,1-difluoro-1-chloroethane which develop leaks that can not be corrected normally may be disposed of by the procedure described in Appendix II-A.

Materials of Construction

Most of the commonly used construction metals, such as steel, cast iron, brass, copper, tin, lead, and aluminum, can be employed with 1,1-difluoro-1-chloroethane under normal conditions of use. However, contact with hot metals may cause decomposition and lead to toxic by-products and cause corrosion, especially if moisture is present.

Piping and vessels to contain 1,1-difluoro-1-chloroethane should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

1,1-Difluoro-1-chloroethane is packaged in DOT approved, low pressure, steel cylinders. Cylinders containing 1,1-difluoro-1-chloroethane are equipped with brass valves with the alternate Compressed Gas Association (CGA) outlet connection No. 660. The valve outlet has a thread size of 1.030 inches, with right-hand external threads, with a flat seat and washer (see Figure 1). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet and a 3/16"-18 threads per inch male dual valve outlet.

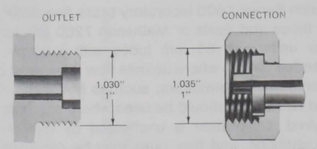


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders containing 1,1-difluoro-1-chloroethane have fusible metal plug safety devices melting point 73.9 °C (165 °F). Cylinders over 30 inches long, exclusive of the neck, require this device in both ends of the cylinder.

Recommended Controls

Automatic Pressure Regulators

Single stage regulator Model 1P-660 is recommended for use with 1,1-difluoro-1-chloroethane. The regulator has a brass body, fabric-reinforced neoprene rubber diaphragm, and neoprene seat. Its delivery pressure range is 28–240 kPa (4–35 psig). No cylinder pressure gauge is necessary since it would not indicate cylinder content but only vapor pressure which will remain constant as long as any liquid remains in the cylinder. Cylinder content should be determined by weighing.

Regulator Model 3321 with a delivery pressure range of 28–410 kPa (4–60 psig) is recommended for use with lecture bottles.

Satisfactory low pressure regulation may be obtained with Matheson Model 70 low pressure regulators, which have oversize, pancake bodies of die cast aluminum and Buna N diaphragms. These are available in three pressure ranges:

	Delivery Pressure Ranges		
Model No.	kPa	mbar (g)	psig
70B-660	0.5–3.0	5–30	2–12 inches water column
70-660	3.4–34.5	34–345	0.5–5.0 psig
70A-660	34.5–68.9	345–689	5–10 psig

To prevent suckback of foreign materials, a check valve is recommended for use with the above regulators.

Manual Controls

Matheson needle valve Model 50-660, a brass bar stock valve, is recommended for direct connection to the cylinder

valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, ¼" compression fitting, or ¼" NPT male or female pipe. It should be used only where manual flow is needed, but this requires close supervision. It should not be used as a pressure control since it will not prevent excessive pressure from developing if the system becomes clogged or is closed. A Model 31B manual needle valve is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

1,1-Difluoro-1-chloroethane is classified by the DOT as a flammable compressed gas and is shipped with the required "Red Gas Label".

Commercial Preparation

1,1-Difluoro-1-chloroethane is obtained by chlorinating 1,1-difluoroethane in the presence of ultraviolet light followed by fractionation.

Chemical Properties

1,1-Difluoro-1-chloroethane may be chlorinated in ultraviolet light to higher chlorinated derivatives. Dehydrohalogenation yields polymerizable unsaturated materials. The presence of 2 fluorine atoms on the same carbon atom imparts considerable resistance to hydrolysis.

Thermodynamic and Detailed Physical Data

Molecular Structure (1)

1,1-Difluoro-1-chloroethane has C_{3v} symmetry, with the following approximate bond distances: C—C 1.45 Å (1.45 × 10^{-10} m); C—F 1.33 Å (1.33 × 10^{-10} m); C—H 1.09 Å (1.09 × 10^{-10} m) (1).

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous 1,1-difluoro-1-chloroethane.

Vapor Pressure

@ 0 °F	149.9 kPa; 1.5 bar; 21.7 psia; 1.179 atm
@ 20 °F	299.1 kPa; 2.99 bar; 43.4 psia; 2.952 atm

For additional vapor pressure data, see Table 1.

Latent Heat of Vaporization, ΔHv (3)

Temperature, °F	ΔHv, kJ/kg
0	217.78
20	205.56

For additional ΔHv values, see Table 1.

Thermodynamic Data

See Table 1 for the thermodynamic properties of saturated 1,1-difluoro-1-chloroethane.

Thermodynamic Properties of 1,1-Difluoro-1-chloroethane As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	82.592 J/(mol·°K)
Entropy, S°	306.855 J/(mol·°K)
Free Energy Function $(G_{298}^\circ - H_0^\circ)/298$	−253.258 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	15.983 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of 1,1-difluoro-1-chloroethane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 119–123, Matheson, Lyndhurst, New Jersey.

[3] L. Riedel, *Bull. Intern. Inst. Refrig. 23*, 1–5 (1942).

[4] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds, 1968*, Volume 1, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[5] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

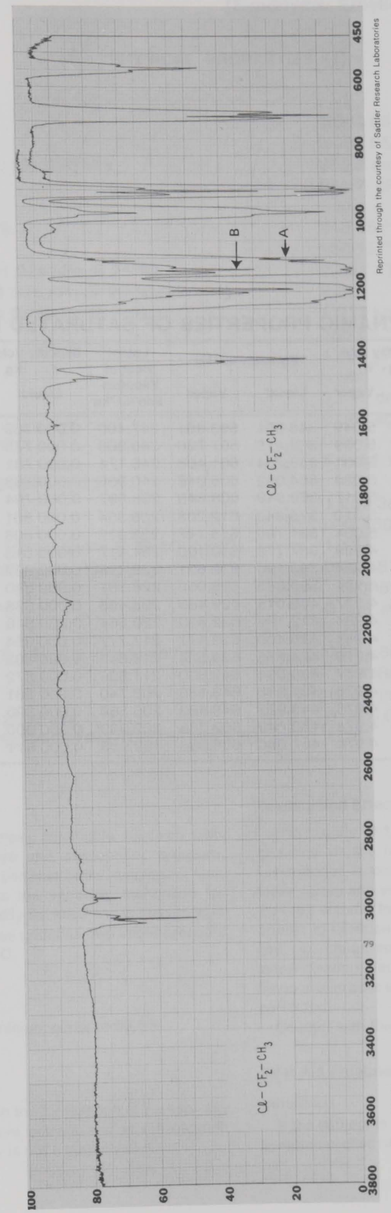


Fig. 2. Infrared spectrum of gaseous H_3CCClF_2 in the 3 800-450 cm^{-1} frequency region; 10 cm cell path length; KBr windows; cell pressure: curve A (complete scan): 2 666 kPa (20 mmHg), curve B (partial scan): 0 533 kPa (4 mmHg) (5).

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED H_3CCCIF_2 (3)

Temperature		Pressure		Entropy kJ/(kg·°K)		Enthalpy kJ/kg		Latent Heat of Vaporization kJ/kg	Specific Volume m^3/kg		Density kg/m^3	
°K	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
222.04	−60	7.498	0.074	3.888	5.049	346.561	593.961	247.400	0.000 769	2.414	1 300.4	0.414 2
224.82	−55	10.335	0.102	3.915	5.039	352.418	597.726	245.308	0.000 775	1.787	1 290.3	0.559 6
227.59	−50	14.084	0.139	3.941	5.031	358.234	601.408	243.174	0.000 781	1.343	1 280.4	0.744 6
230.37	−45	18.846	0.186	3.967	5.023	364.092	605.048	240.956	0.000 788	1.024	1 269.0	0.976 6
233.15	−40	24.825	0.245	3.993	5.017	369.949	608.646	238.697	0.000 794	0.791	1 259.4	1.264
235.93	−35	32.323	0.319	4.018	5.010	375.849	612.203	236.354	0.000 801	0.620	1 248.4	1.613
238.71	−30	41.442	0.409	4.043	5.004	381.790	615.717	233.927	0.000 808	0.491	1 237.6	2.037
241.48	−25	52.689	0.520	4.067	4.999	387.773	619.190	231.417	0.000 815	0.393	1 227.0	2.545
244.26	−20	66.165	0.653	4.091	4.994	393.798	622.621	228.823	0.000 822	0.317	1 216.5	3.155
247.04	−15	82.276	0.812	4.115	4.991	399.865	626.052	226.187	0.000 830	0.259	1 204.8	3.861
249.82	−10	101.426	1.001	4.138	4.987	406.015	629.483	223.468	0.000 838	0.213	1 193.3	4.695
252.59	−5	123.819	1.222	4.161	4.984	412.166	632.830	220.664	0.000 846	0.177	1 182.0	5.650
255.37	0	149.860	1.479	4.184	4.981	418.400	636.177	217.777	0.000 854	0.148	1 171.0	6.757
258.15	5	180.055	1.777	4.207	4.979	424.676	639.524	214.848	0.000 863	0.124	1 158.7	8.065
260.93	10	214.708	2.119	4.229	4.977	430.994	642.830	211.836	0.000 872	0.105	1 146.8	9.524
263.71	15	254.326	2.510	4.252	4.976	437.395	646.135	208.740	0.000 881	0.090	1 135.1	11.111
266.48	20	299.111	2.952	4.274	4.975	443.922	649.482	205.560	0.000 890	0.077	1 123.6	12.987
269.26	25	349.774	3.452	4.296	4.974	450.449	652.788	202.339	0.000 900	0.066	1 111.1	15.152
272.04	30	406.617	4.013	4.317	4.974	457.060	656.093	199.033	0.000 911	0.057	1 097.7	17.544

1,1-DIFLUOROETHANE

(Synonyms: Ethylidene Fluoride; Genetron-152A®)
(Formula: H_3CCHF_2 or $C_2H_4F_2$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.066 051 kg
One Mole of $C_2H_4F_2$	0.066 051 kg
Specific Volume @ 21.1 °C, 101.325 kPa	365.2 dm^3/kg; 5.85 ft^3/lb
Vapor Pressure @ 21.1 °C	535.7 kPa; 5.36 bar; 77.7 psia; 5.29 atm
Boiling Point @ 101.325 kPa	248.45 °K; −24.7 °C; −12.5 °F
Freezing Point	156.15 °K; −117.0 °C; −178.6 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	2.701 4 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	2.28
Density, Liquid @ Saturation Pressure @ −26.0 °C	1.012 kg/l
Critical Temperature	386.65 °K; 113.5 °C, 236.3 °F
Critical Pressure	4 496 kPa; 44.96 bar; 652.1 psia; 44.37 atm
Critical Volume	2.742 dm^3/kg
Critical Density	0.365 kg/dm^3
Critical Compressibility Factor	0.253
Flammability Limits in Air	5.1–17.1% (by volume)
Specific Heat Gas @ 101.325 kPa @ 25 °C	
@Constant Pressure	1 059.389 J/(kg·°K)
@ Constant Volume	933.450 J/(kg·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.135
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.008 87 mPa·s; 0.008 87 mN·s/m^2; 0.008 87 cP
Viscosity, Liquid @ −30.6 °C	0.369 mPa·s; 0.369 mN·s/m^2; 0.369 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.011 84 W/(m·°K); 28.3 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 20 °C	11.25 mN/m; 11.25 dyn/cm
Solubility in Water @ 101.325 kPa @ 0 °C	0.54% (by weight)
Refractive Index, Liquid @ Saturation Pressure, n_D @ 25 °C	1.25

Description

1,1-Difluoroethane is a colorless, flammable, relatively non-toxic gas at room temperature and atmospheric pressure. Cylinders, truck cargo tanks, portable tanks, single-unit tank cars, and ton multi-unit tanks are variously authorized for shipment of H_3CCHF_2. It is readily liquefied and is reshipped in steel cylinders as a liquefied gas under its own vapor pressure of 434 kPa (63 psig) at 21.1 °C.

Specifications

1,1-Difluoroethane has a minimum purity of 98.0%.

Uses

1,1-Difluoroethane is used in the formulation of aerosol dispersants, as a low temperature solvent and in refrigeration systems where its flammability is not a major factor.

Toxicity and Effects in Man (2)

The toxicity of 1,1-difluoroethane is very low. Its estimated grouping via the rating system devised by the Underwriters' Laboratories is probably Group 6 a category which includes those gases and vapors which in concentrations up to at least 20% by volume for durations of exposure of 2 hours do not appear to produce injury. Inhalation of high concentrations of gas can cause such symptoms as dizziness, disorientation, incoordination, narcosis, nausea or vomiting. There appear to be no irreversible effects once the oxygen deficiency has been corrected.

Contact with the liquid state may cause frostbite.

First Aid Treatment (2)

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated

area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration and oxygen simultaneously. Treat symptomatically thereafter.

Skin Contact

In case of skin contact with liquid 1,1-difluoroethane, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The hazard involved in the handling of the material is due to its flammability. Ground all equipment and cylinders of the gas before use. Store and use cylinders in well-ventilated areas away from heat and all sources of ignition such as flames and sparks. Never use flames to detect leaks, use soap water solution. Do not use the gas around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of cylinders with cylinders containing oxygen, chlorine or other highly oxidizing and flammable materials.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks of 1,1-difluoroethane may be detected by applying soap water solution to suspected points; leaks will be indicated by bubble formation.

Disposal of Leaking Cylinders

Cylinders containing 1,1-difluoroethane which develop leaks that cannot be corrected normally may be disposed of by the procedure outlined in Appendix II-A.

Materials of Construction

Most of the commonly used construction metals, such as steel, cast iron, brass, copper, tin, lead or aluminum can be employed with 1,1-difluoroethane under normal conditions of use. However, contact with hot metals may cause decomposition and lead to toxic by-products and cause corrosion, especially if moisture is present.

Piping and vessels should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

1,1-Difluoroethane is packaged in DOT approved, low pressure steel cylinders. Cylinders containing 1,1-difluoroethane are equipped with brass valves with the approved alternate Compressed Gas Association (CGA) outlet connection No. 660. The valve outlet has a thread size of 1.030 inches, with right-hand external threads, with a flat seat and washer (see Figure 1). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet and a 9/16-18 threads per inch male dual valve outlet.

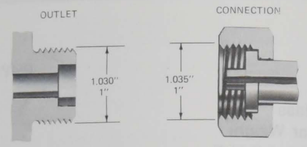


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders containing 1,1-difluoroethane have fusible metal plug safety devices, melting at about 73.9 °C (165 °F). Cylinders over 30 inches long (exclusive of the neck) require this device in both ends of the cylinder.

Recommended Controls

Automatic Pressure Regulator

Single stage regulator Model 1P-660 is recommended for use with 1,1-difluoroethane. The regulator has a brass body neoprene rubber diaphragm and neoprene seat. Its delivery pressure range is 28-240 kPa (4-35 psig). No cylinder pressure gauge is necessary since it would not indicate cylinder content but only vapor pressure which will remain constant as long as any liquid remains in the cylinder. Cylinder content should be determined by weighing.

Regulator Model 3321 with a delivery pressure range of 28-410 kPa (4-60 psig) is recommended for use with lecture bottles.

Satisfactory low pressure regulation may be obtained with Matheson Model 70 low pressure regulators, which have oversize, pancake bodies of die cast aluminum and Buna N diaphragms. These are available in three pressure ranges:

	Delivery Pressure Range		
Model No.	kPa	mbar (g)	psig
70B-660	0.5–3.0	5–30	2–12 inches water column
70-660	3.4–34.5	34–345	0.5–5.0 psig
70A-660	34.5–68.9	345–689	5–10 psig

To prevent suckback of foreign materials, a check valve is recommended for use with the above regulators.

Manual Controls

Matheson needle valve Model 50-660, a brass bar stock valve is recommended for direct connection to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, 1/4" compression fitting, or 1/4" NPT male or female pipe. It should be used only where manual flow is needed, but this requires close supervision. It should not be used as a pressure control since it will not prevent excessive pressure from developing if the system becomes clogged or is closed. A Model 31B manual needle valve is recommended for use with lecture bottles.

Matheson

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

1,1-Difluoroethane is classified by the DOT as a flammable compressed gas, taking a "Red Gas Label".

Commercial Preparation

1,1-Difluoroethane is obtained by the addition of hydrogen fluoride to acetylene in liquid hydrogen fluoride with boron trifluoride as a catalyst.

Chemical Properties

1,1-Difluoroethane is very stable toward hydrolysis. It may be chlorinated in sunlight to give isomeric monochloro derivatives and some more highly chlorinated products. Dehydrofluorination yields polymerizable unsaturated products.

Thermodynamic and Detailed Physical Data

Infrared Spectrum

See Figure 2 for the infrared spectrum of 1,1-difluoroethane.

Vapor Pressure (3)

The vapor pressure of liquid H_3CCHF_2 between 180.15 °K and 265.15 °K is represented by the following Antoine vapor pressure equation:

$$\log_{10} p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which t = °C and p = mmHg and the constants A, B, and C have the values of 7.030, 910.0, and 244.0, respectively.

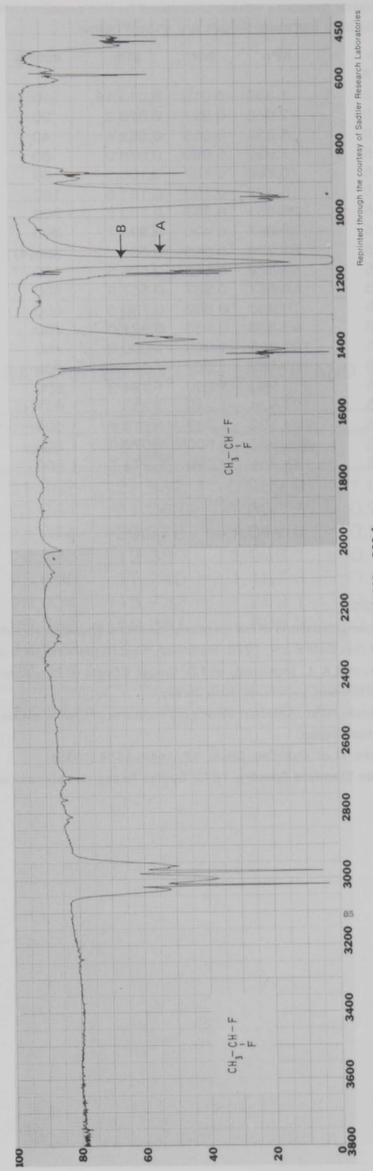


Fig. 2. Infrared spectrum of gaseous, 1,1-difluoroethane over the frequency range 3 800–450 cm^{-1}, 10 cm path length cell, with KBr windows; cell pressure; curve A (complete scan): 3.33 kPa (25 mmHg), curve B (partial scan): 0.0667 kPa (0.5 mmHg) (5).

Matheson

Some vapor pressure values calculated by this equation and some additional literature values are shown below:

Temperature, °K	kPa	bar	atm	mmHg
180.15	1.333	0.013	0.013 16	10
188.15	2.666	0.027	0.026 3	20
197.15	5.333	0.053	0.052 6	40
202.15	7.999	0.080	0.078 9	60
206.15	10.666	0.107	0.105 3	80
210.15	13.332	0.133	0.131 6	100
221.55	26.664	0.267	0.263 2	200
229.05	39.997	0.400	0.394 7	300
233.15	51.270	0.513	0.506	385(4)
234.65	53.329	0.533	0.526 3	400
239.25	66.661	0.667	0.657 9	500
243.15	79.993	0.800	0.789 5	600
246.55	93.326	0.933	0.921 0	700
248.45	101.325	1.013	1.000 0	760
249.65	106.658	1.067	1.052 6	800
252.45	119.990	1.200	1.184 2	900
253.15	124.934	1.249	1.233	937(4)
255.15	133.322	1.333	1.315 8	1 000
259.15	159.987	1.600	1.578 9	1 200
265.15	199.984	2.000	1.973 7	1 500

For vapor pressure values at higher temperatures, see Table 1 and Figure 3.

Latent Heat of Vaporization, ΔHv @ −24.7 °C 321.92 kJ/kg; 76.94 kcal/kg

For additional ΔHv values, see Table 1.

Thermodynamic Data

For the thermodynamic properties of saturated 1,1-difluoroethane, see Table 1.

Thermodynamic Properties of 1,1-Difluoroethane as Ideal Gas @ 25 °C (3)

Heat Capacity, C_p^o	67.906 J/(mol·°K)
Entropy, S^o	282.504 J/(mol·°K)
Free Energy Function, $(G_{298}^o - H_0^o)/298$	−235.601 J/(mol·°K)
Enthalpy Function, $(H_{298}^o - H_0^o)/298$	46.861 J/(mol·°K)
Enthalpy Difference, $H_{298}^o - H_0^o$	13.975 kJ/mol

REFERENCES

For extensive tabulations of the thermodynamic and physical properties of 1,1-difluoroethane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, and A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 119–123, Matheson, Lyndhurst, New Jersey.

[3] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds, 1968*, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[4] W. H. Mears, *et al.*, *Ind. Eng. Chem.* 47, 1449–1454 (1955).

[5] **The Sadtler Standard Spectra,** *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED H_3CCHF_2 LIQUID AND VAPOR (4)

Temperature, °K	Pressure kPa	Pressure atm	Enthalpy kJ/mol Liquid	Enthalpy kJ/mol Vapor	Latent Heat of Vaporization kJ/mol	Specific Volume dm^3/kg Liquid	Density kg/dm^3 Liquid
233.15	51.270	0.506	0.000	21.882	21.882	0.959 9	1.041 8
253.15	124.934	1.233	1.791	23.054	21.263	1.000 7	0.999 3
273.15	267.093	2.636	3.598	23.974	20.376	1.044 6	0.957 1
293.15	514.731	5.080	5.607	24.937	19.330	1.096 1	0.912 3
313.15	912.128	9.002	7.950	25.690	17.740	1.167 3	0.856 7
333.15	1 330.678	14.902	10.502	26.234	15.732	1.252 1	0.798 7
353.15	2 442.130	23.292	13.472	26.359	12.887	1.388 3	0.720 3
373.15	3 597.04	34.69	16.945	25.522			
386.65	4 495.79	44.37	23.012	23.012			

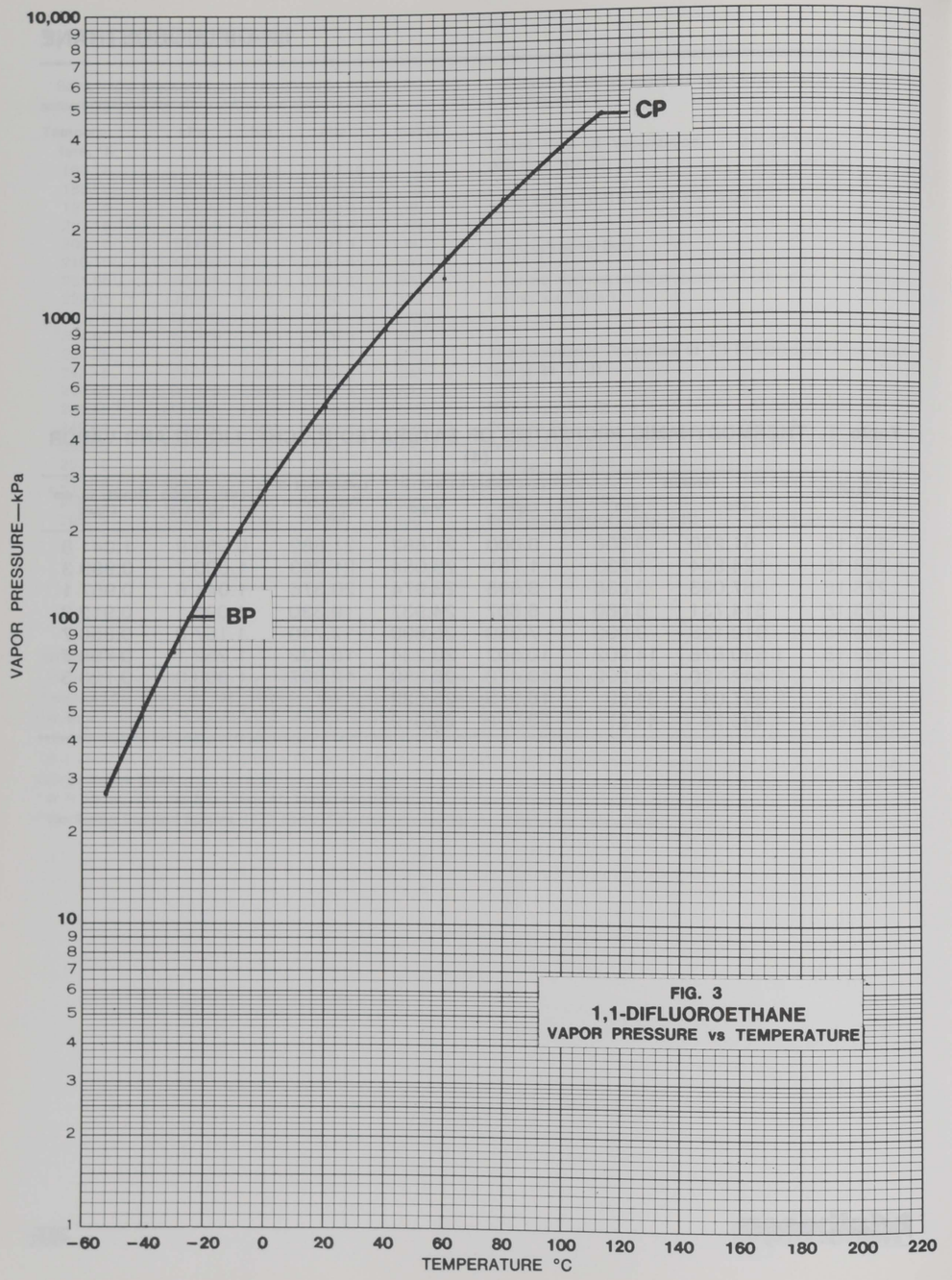


FIG. 3
1,1-DIFLUOROETHANE
VAPOR PRESSURE vs TEMPERATURE

1,1-DIFLUOROETHYLENE

(Synonyms: Vinylidene Fluoride; Genetron-1132A®)
(Formula: $H_2C:CF_2$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.064 035 kg
One Mole of $H_2C:CF_2$	0.064 035 kg
Specific Volume @ 21.1 °C, 101.325 kPa	374.6 dm^3/kg; 6 ft^3/lb
Vapor Pressure @ 21.1 °C	3 571.5 kPa; 35.7 bar; 532.7 psia; 35.25 atm
Boiling Point @ 101.325 kPa	187.45 °K; −85.7 °C; −122.3 °F
Freezing Point	129.15 °K; −144.0 °C; −227.2 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	2.619 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C	2.21
Density, Liquid @ Saturation Pressure @ −60 °C	1.040 kg/l
Critical Temperature	302.85 °K; 29.7 °C; 85.5 °F
Critical Pressure	4 458.3 kPa; 44.58 bar; 646.6 psia; 44.0 atm
Critical Volume	2.405 dm^3/kg
Critical Density	0.416 kg/dm^3
Critical Compressibility Factor	0.273
Flammability Limits In Air	5.5–21.3% (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	60.124 J/(mol·°K); 0.224 kcal/(kg·°C)
Specific Heat, Liquid @ −100 °C	991.61 J/(kg·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.012 45 mPa·s; 0.012 45 $mN·s/m^2$; 0.012 45 cP
Viscosity, Liquid @ −100 °C	0.230 mPa·s; 0.230 $mN·s/m^2$; 0.230 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.013 6 W/(m·°K); 32.5 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −100 °C	22.0 mN/m; 22.0 dyn/cm
Solubility in Water @ 101.325 kPa @ 25 °C	6.3 cm^3/0.1 kg
Autoignition Temperature	913 °K; 640 °C; 1 184 °F

Description

1,1-Difluoroethylene is a colorless, flammable, nontoxic gas at room temperature and atmospheric pressure. It has a faint ethereal odor. Cylinders, truck cargo tanks, portable tanks, single-unit tank cars and ton multi-unit tanks are variously authorized for shipment of $H_2C:CF_2$. It is reshipped in steel cylinders as a liquefied gas under its own vapor pressure of 3570 kPa (517 psig) at 21.1 °C.

Specifications

1,1-Difluoroethylene has a minimum purity of 99.0%.

Uses

1,1-Difluoroethylene is used for the preparation of polymers and copolymers, and as an intermediate in organic synthesis.

Toxicity

Rats exposed for 19 hours to an 80% concentration by volume of 1,1-difluoroethylene and 20% oxygen showed no loss of reflexes. 1,1-Difluoroethylene appears to have no substantial toxicity.

Precautions in Handling and Storage

The hazards associated with the use of 1,1-difluoroethylene stem mainly from its flammability. Store and use 1,1-difluoroethylene cylinders in well-ventilated areas away from heat and all sources of ignition such as flames and sparks. Never use flames to detect flammable gas leaks, use soapy water. Do not use 1,1-difluoroethylene around sparking motors or other nonexplosion-proof equipment. Do not store reserve stocks of 1,1-difluoroethylene cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all lines used with 1,1-difluoroethylene.

In addition, the general rules given in Appendix I should be observed.

Leak Detection

Leaks of 1,1-difluoroethylene in lines or equipment may be detected by painting the suspected sites with soap water. Leaks will be indicated by bubble formation.

Never use a flame to detect leaks.

Disposal of Leaking Cylinders

Cylinders containing 1,1-difluoroethylene which develop leaks that cannot be corrected normally may be disposed of by the method described in Appendix II-A.

Materials of Construction

Since 1,1-difluoroethylene is a noncorrosive gas, any common or commercially available metal may be used. However, piping systems or vessels to contain 1,1-difluoroethylene should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

1,1-Difluoroethylene is shipped in DOT approved steel cylinders. The cylinder is equipped with valves having the approved alternate Compressed Gas Association (CGA) valve outlet No. 320 which has a thread size of 0.825 inch diameter, right-hand external threads, with a flat seat using a washer as a seal (see Figure 1). Lecture bottles have a special 5/16 inch-32 threads per inch female outlet and a 9/16"-18 threads per inch, male dual valve outlet.

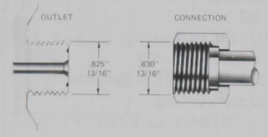


Fig. 1. CONNECTION 320 .825"-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders of 1,1-difluoroethylene have frangible discs as safety devices. Cylinders should, therefore, be stored away from sources of heat to avoid developing pressures capable of rupturing the disc.

Recommended Controls

To reduce the high cylinder pressure of 1,1-difluoroethylene to a safe working value consistent with a system's design, the following types of controls are recommended.

Automatic Pressure Regulators

1. Single Stage Regulators

A single stage regulator will reduce cylinder pressure in one stage to a delivery pressure in a particular range, depending upon the design of the regulator and its spring load. A single stage regulator will show a variation in delivery pressure as cylinder pressure falls. The following Matheson single stage regulators are recommended for use with 1,1-difluoroethylene:

Model No.	Delivery Pressure Range kPa	bar (g)	psig
1P-320	28–240	0.28–2.4	4–35
1L-320	28–550	0.28–5.5	4–80
1H-320	69–1240	0.69–12.4	10–180
2-320	340–4480	3.4–44.8	50–650
3321 (with lecture bottles)	28–410	0.28–4.1	4–60

2. Two Stage Automatic Regulators

This type of regulator performs the same function as a single stage regulator. However, greater accuracy in control of delivery pressure is maintained and the delivery pressure does not vary as cylinder pressure falls. The following Matheson two stage regulators are recommended for use with 1,1-difluoroethylene:

Model No.	Delivery Pressure Range kPa	bar (g)	psig
8L-320	14–104	0.14–1.04	2–15
8-320	28–340	0.28–3.4	4–50
8H-320	69–690	0.69–6.9	10–100
9-320	138–1720	1.38–17.2	20–250

To prevent suckback of foreign materials, a check valve is recommended for use with the above regulators.

Manual Controls

Matheson needle value Model 50-320, a brass bar stock valve, is recommended for direct connection to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, ¼" compression fitting, or ¼" NPT male or female pipe. It should be used only where manual flow is needed, but this requires close supervision. It should not be used as a pressure control since it will not prevent excessive pressure from developing if the system becomes clogged or is closed. A Model 31B manual needle valve is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Matheson

Shipping Regulations

1,1-Difluoroethylene is shipped in high pressure steel cylinders as a flammable compressed gas, requiring DOT "Red Gas Label".

Commercial Preparation

U.S. 2,734,090 (2) describes the preparation of 1,1-difluoroethylene in 43% yield by passing a mixture of 6 moles of hydrogen and 33 moles of CF_2ClCH_2-Cl over nickel wire at 490–500 °C with a contact time of 10 seconds. It has also been obtained by dehydrochlorination of 1-chloro-1,1-difluoroethane (3).

Chemical Properties

1,1-Difluoroethylene exhibits the general properties of olefins. It undergoes polymerization and copolymerization. It is shipped without an inhibitor since inhibition was found to be unnecessary under normal cylinder storage conditions.

Thermodynamic and Detailed Physical Data

Molecular Structure (1)

1,1-Difluoroethylene has D_{2h} symmetry and a symmetry number of four, with the following approximate bond distances and bond angle: C-F 1.313 Å (1.313×10^{-10} m); C = C 1.313 Å (1.313×10^{-10} m); F-C-F 114°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous 1,1-difluoroethylene.

Vapor Pressure (4)

Vapor pressure values above 1 atm have been calculated by the formula $\log_{10}P = A - B/T$, in which P = lbf/in² absolute (psia) and T = °K, and the constants A and B have the values of 5.463 and 805, respectively.

The following values have been calculated by this equation:

Temperature, °K	Vapor Pressure kPa	bar	psia	mmHg
223.15	495.04	4.95	71.8	3 716
233.15	706.02	7.06	102.4	5 297
253.15	1 323.79	13.24	192.0	9 956
273.15	2 262.86	22.63	328.2	16 948
283.15	2 875.11	28.75	417.0	21 584
293.15	3 594.93	35.95	521.4	26 980
298.15	3 996.89	39.97	579.7	29 944
302.85	4 401.61	44.02	638.4	32 984
303.25	4 433.33	44.33	643.0	33 288

For vapor pressure curve, see Figure 3.

Vapor pressure data below 1 atm are listed below (5).

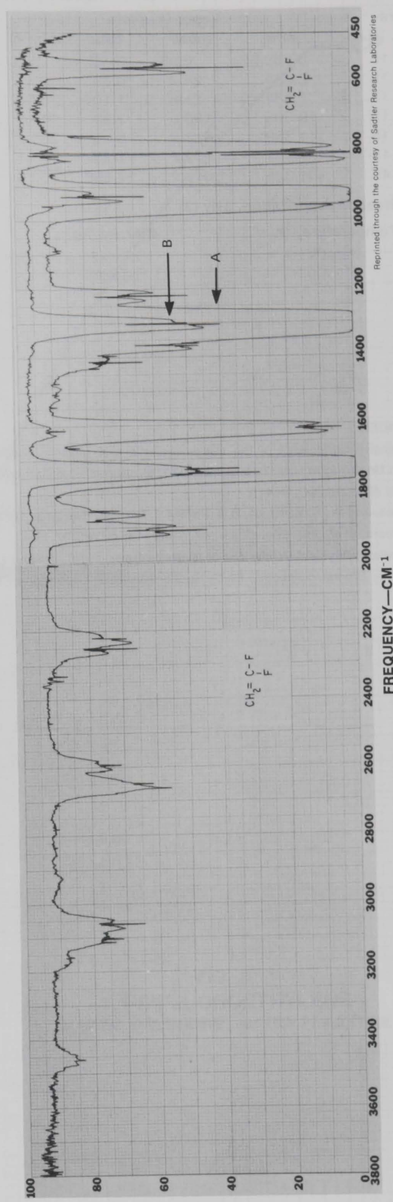


Fig. 2. Infrared spectrum of gaseous 1,1-difluoroethylene over the frequency range 3 800–450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure: curve A (complete scan): 2.667 kPa (20 mmHg); curve B (partial scan): 0.533 kPa (4 mmHg) (6).

Matheson

1,1-DIFLUOROETHYLENE

Temperature, °K	Vapor Pressure kPa	mbar	psia	mmHg
133.15	0.689 5	6.93	0.10	5.2
143.15	2.689	26.9	0.39	20.1
153.15	7.584	75.8	1.10	57.0
163.15	19.305	193.0	2.80	145.2
173.15	41.369	413.7	6.00	310.2
183.15	77.221	772.2	11.20	579.1
187.45	101.325	1 013.25	14.696	760.0

Latent Heat of Vaporization, ΔHv (3)

Temperature, °K	ΔHv, kJ/kg
153.15	271.12
173.15	257.32
193.15	243.51
213.15	230.12

Thermodynamic Data

Thermodynamic Properties of 1,1-Difluoroethylene As Ideal Gas @ 25 °C (1)

Heat Capacity, C_p°	57.61 J/(mol·°K)
Entropy, S°	266.10 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	12.468 kJ/mol
Enthalpy, H_{298}°	17.55 kJ/mol
Enthalpy of Formation, ΔH_f°	−328.86 kJ/mol
Free Energy of Formation, ΔF_f°	−305.43 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of 1,1-difluoroethylene, see W. Braker and A. L. Mossman, **The Matheson Unabridged Gas Data Book, 1975**, Matheson, East Rutherford, New Jersey.

[2] Chemical Abstracts 50, 9441h.

[3] R. Mantell, and W. S. Barnhart, **U.S. Patent 2,774,799** (Dec. 18, *1956* to M. W. Kellogg Co.).

[4] M. H. Mears, *et al., Ind. Eng. Chem.* 47, 1449–1454 (1955).

[5] R. W. Gallant, **Physical Properties of Hydrocarbons**, *1968*, Volume 1, pp. 202–209, Gulf Publishing Co., Houston, Texas.

[6] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Matheson

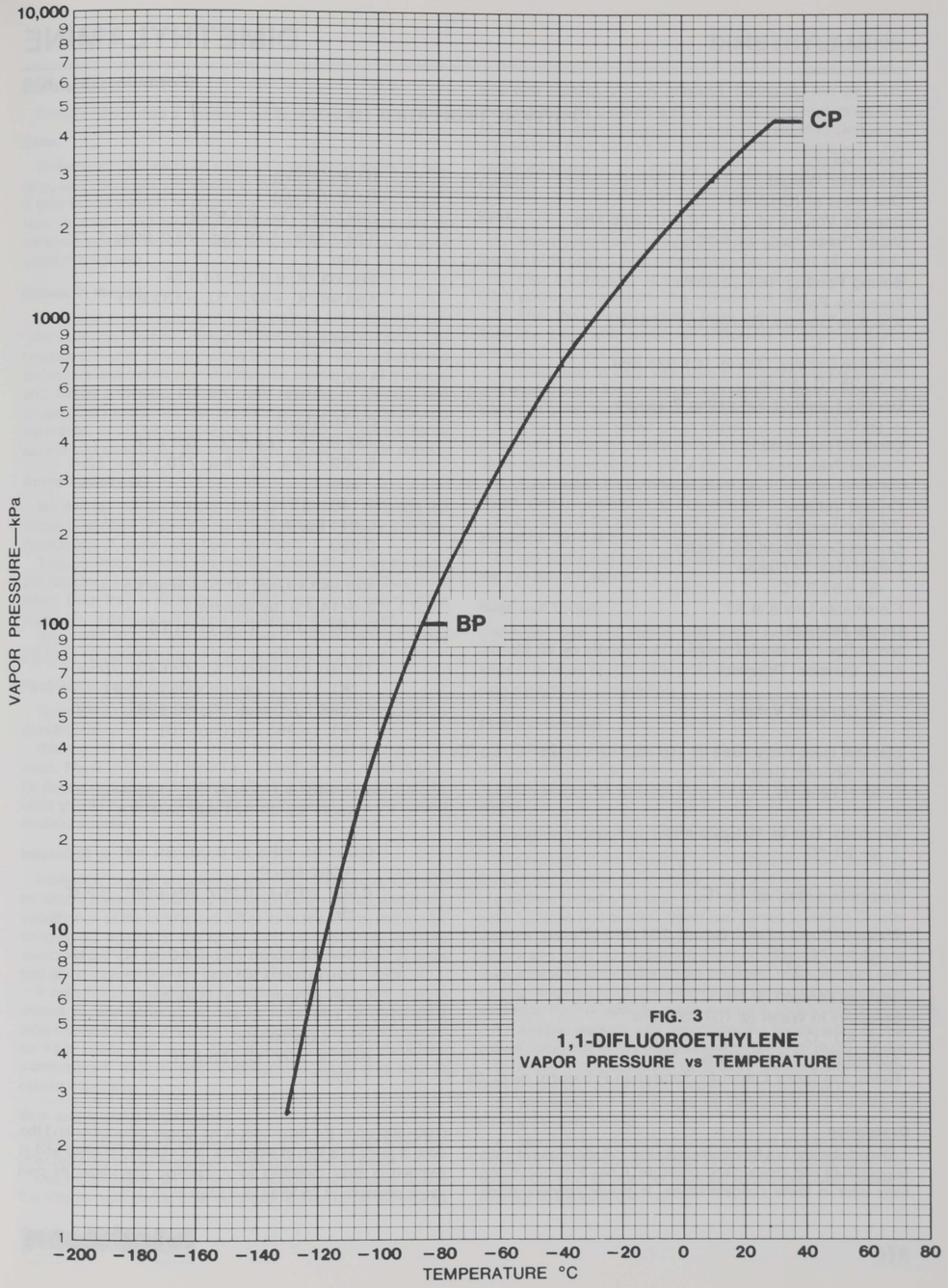


FIG. 3
1,1-DIFLUOROETHYLENE
VAPOR PRESSURE vs TEMPERATURE

DIMETHYLAMINE

(Formula: $(CH_3)_2NH$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.045 085 kg
One mole of $(CH_3)_2NH$	0.045 085 kg
Specific Volume @ 21.1 °C, 101.325 kPa	536.9 dm^3/kg; 8.6 ft^3/lb
Vapor Pressure @ 21.1 °C	179.3 kPa; 1.79 bar; 26.0 psia; 1.77 atm
Boiling Point @ 101.325 kPa	280.03 °K; 6.9 °C; 44.4 °F
Freezing Point	180.96 °K; −92.2 °C; −133.9 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	1.844 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.557
Density Liquid @ Saturation Pressure @ 0 °C	0.678 6 kg/l
Critical Temperature	437.80 °K; 164.6 °C; 328.4 °F
Critical Pressure	5 309.4 kPa; 53.1 bar; 770.1 psia; 52.4 atm
Critical Volume	4.148 dm^3/kg
Critical Density	0.241 kg/dm^3
Critical Compressibility Factor	0.280
Latent Heat of Fusion @ −92.2 °C	131.943 kJ/kg; 31.514 kcal/kg
Flammable Limits in Air	2.8–14.4% (by volume)
Dipole Moment	3.369×10^{-30} C.m; (1.01 D)
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	72.040 kJ/(kmol·°K); 72.040 J/(mol·°K); 17.218 cal/(mol·°C)
@ Constant Volume	62.698 kJ/(kmol·°K); 62.698 J/(mol·°K); 14.985 cal/(mol·°C)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.149
Molar Specific Heat, Liquid @ −12.4 °C	135.440 kJ/(kmol·°K); 135.440 J/(mol·°K); 32.371 cal/(mol·°C)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.007 55 mPa·s; 0.007 55 $mN \cdot s/m^2$; 0.007 55 cP
Viscosity, Liquid @ 15 °C	0.207 mPa·s; 0.207 $mN \cdot s/m^2$; 0.207 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.014 23 W/(m·°K): 34.0×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 15 °C	17.61 mN/m; 17.61 dyn/cm
Solubility In Water @ 101.325 kPa @ 60 °C	23.7% (by weight)
Autoignition Temperature	675 °K; 402 °C; 755.6 °F
Refractive Index Liquid @ Saturation Pressure, n_D @ 25 °C	1.356 6

Description

Dimethylamine is a flammable, alkaline, colorless gas at room temperature and atmospheric pressure. It has a characteristic fishy odor in lower concentrations. In higher concentrations (100–500 ppm) the fishy odor is no longer detectable and the odor is more like that of ammonia. It is readily liquefied and is shipped in steel cylinders as a liquefied gas under its own vapor pressure of 78 kPa (11.3 psig) at 21.1 °C.

Specifications

Dimethylamine has a minimum purity of 99.0%.

Uses

Dimethylamine has been used as a dehairing agent in tanning; as an acid gas absorbent; in dyes; as a flotation agent; as a gasoline stabilizer; in pharmaceuticals; in rubber accelerators; in soaps and cleaning compounds; in the treatment of cellulose acetate rayon; in organic syntheses; and as an agricultural fungicide.

Effects in Man (2)

Exposure to the vapors of these amines produces eye irritation with lacrimation, conjunctivitis and corneal edema. Inhalation of higher concentrations (more than 100 ppm) of these amines causes irritation of the mucous membrane of the nose and throat and lung irritation with respiratory distress and cough. The vapors may also produce primary skin irritation and dermatitis. Direct local contact with the liquid amines produces severe and sometimes permanent eye damage or skin burns.

Acute Toxicity (2)

No definite human toxicity data are available, although the above described physiological effects from relatively low concentrations of vapor have been recorded.

Though these amines are readily detectable in air by odor, the olfactory sense may become fatigued on continuous inhalation. Odor then is no longer a reliable warning property of the presence of dangerous concentrations of these vapors.

The 1979 ACGIH has established a Threshold Limit Value (TLV) of 10 ppm (18 mg/m^3) for dimethylamine in air.

First Aid Suggestions (2)

Summon a physician for anyone overcome or injured by dimethylamine.

Prior to the physician's arrival first aid should be started at once. Those presented herein are based on what is believed to be common practice in industry. Their adoption in any specific case should be subject to prior endorsement by a competent medical advisor.

Inhalation

Inhalation causes irritation of the nose and throat, followed by violent sneezing, burning sensation of the throat, coughing, constriction of the larynx and difficulty in breathing, pulmonary congestion, edema of the lungs, and conjunctivitis. Workers overcome by the gas should be removed to fresh air at once and given oxygen therapy until the arrival of a physician.

If breathing has stopped, artificial respiration and oxygen should be administered. It may be necessary to introduce a tube into the throat if the larynx is closed. The patient should be kept warm and quiet. No alcoholic stimulant should be administered. Oxygen and antispasmodic drugs may help to relieve coughing.

Skin and Mucous Membranes

Strip contaminated clothing from the body and flood the affected area of the body with large quantities of water.

Use no ointments on the skin or mucous membranes during the first 24 hour period after the injury. Do not cover the injured area with clothing or a dry dressing. During the first 24 hours the area may be covered with a dressing and kept moist with physiological salt solution (0.9% sodium chloride.) Dermatitis is produced from contact of dimethylamine with the skin. For persistent cases of skin irritation a physician should be consulted.

Eyes

1. Immediately flush the eyes thoroughly with water, holding the lids wide open. Continue irrigation for at least 15 minutes.
2. After the irrigation is completed, instill 2 or 3 drops of a 0.5% pontocaine solution. This relieves the pain.
3. After the pain disappears (may require a few minutes), flush the eyes with water, or preferably physiological salt solution (0.9% NaCl).
4. Then drop in each eye 1 drop of fluorescein (eyestain) and wash the eye for 2 minutes with water. If the eye has been injured, a green stain will appear over the injured area.
5. If the eye ball stains green anywhere, put 1 more drop of pontocaine in the eye, wash the eye for 15 minutes (as shown under item 3) and restain with a drop of fluorescein (item 4).
6. Again wash for 2 minutes (item 3). If the eye still stains green, take the patient to an eye specialist.

After items 1 through 6 have been completed, the patient should be taken to an eye specialist without delay.

Do not apply eye pads or pressure, as gluing of the lids to the eye ball will occur.

Nose and Throat

Irrigate nose and mouth with water continuously for 15 minutes. If the patient can swallow, encourage him to drink large quantities of ½% citric acid solution or lemonade. Summon a physician immediately.

First Aid Supplies

In addition to emergency protective equipment, it is recommended that dimethylamine users keep ½% citric acid available in clean, accessible cabinets in an area not likely to be contaminated.

Precautions in Handling and Storage

The hazards in the handling of dimethylamine are due to its toxicity and extreme flammability. Store and use dimethylamine in a well-ventilated area away from heat and all ignition sources such as flame and sparks. Never use flames to detect dimethylamine leaks. Do not use dimethylamine around sparking motors and other non-explosion-proof equipment. Do not store reserve stocks of dimethylamine cylinders with cylinders containing oxygen, chlorine or other highly oxidizing or flammable materials. Further specific precautions are as follows:

1. Anyone working with dimethylamine should wear rubber gloves, chemical safety goggles and a rubber or plastic apron.
2. A gas mask, approved by NIOSH, showers and an eyebath should be conveniently located for emergency use.
3. Withdrawal of gas should be performed in a well-ventilated area or in a hood.
4. Manifolded cylinders of dimethylamine should have check valves at the cylinder outlets to prevent the exchange of material from one cylinder to another; exchange could cause a cylinder to become overfull.

5. A trap or check valve should be used to prevent suckback of foreign materials into the cylinder. This can cause an extremely corrosive condition to form within the cylinder, aside from the possibility of having a violent reaction occur within the cylinder. Any accidental suckback should be reported immediately to the supplier.

6. Ground all equipment and lines used with dimethylamine.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Never use flames to detect dimethylamine leaks. Leaks can be detected by passing an open bottle or a squeeze bottle containing hydrochloric acid in the vicinity of the suspected leak. Wet red litmus or phenolphthalein paper will undergo a color change with dimethylamine and is of aid in detecting small leaks.

Serious leaks which cannot be stopped should be doused with water which will dissolve the dimethylamine and prevent the atmosphere from becoming contaminated.

Cylinder valves may develop leaks through the packing which can be stopped by tightening up on the packing nut, by turning it counter clockwise as viewed from above. Leaks through the valve outlet that cannot be controlled should be stopped by plugging the outlet with ⅜" pipe plugs. If leaks persist, contact the supplier for information on how to remedy the problem.

Disposal of Leaking Cylinders

Cylinders containing dimethylamine which develop leaks that cannot be stopped may be disposed of by the procedure given in Appendix II-B.

Materials of Construction

Iron and steel are recommended for all equipment coming in contact with dimethylamine. Copper, tin, zinc, and their alloys are attacked by moist dimethylamine and should not be used. Piping should be rigid steel except where short connections are required such as between cylinders and manifold or pipe lines.

For permanent installations, tongue and groove, flanged fittings with lead or asbestos composition gaskets are recommended. In order to reduce maintenance all joints should be welded wherever possible.

Cylinder and Valve Description

Cylinder valves are made of forged steel and are of the packed type. The valve outlet designated as alternate standard for dimethylamine by the Compressed Gas Association (CGA) is connection No. 240. The thread specifications are ⅜"-18 NGT-RH-INT accepting tapered threaded pipe. (See Figure 1 for the drawing and specifications of this valve outlet and its mating connection). Lecture bottles have a special 5/16"-32 threads per inch, female valve outlet.

Cylinders containing 15 lb or more dimethylamine are equipped with goose neck dip-tubes. Withdrawal of vapor is accomplished by placing the cylinder in its normal vertical position. On occasion, a full cylinder standing in the sun will heat up and cause the liquid to expand and cover the end of the dip-tube. In this case, it is necessary to allow the cylinder

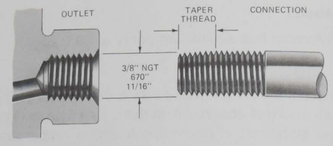


Fig. 1. CONNECTION 240 3/8"-NGT RH INT. IPS accepting Tapered Threaded Pipe

to cool before the vapor can be withdrawn or the cylinder should be placed in a horizontal position with the valve outlet facing down.

To withdraw liquid the cylinder should be placed in a horizontal position with the valve outlet facing up.

Safety Devices

Since no safety devices are used in dimethylamine cylinders, extra precautions should be used to prevent cylinders from being exposed to heat, which could cause uncontrolled hydrostatic pressure build-up.

Recommended Controls

Automatic Pressure Regulators

Single stage regulator Model 13-240 is available for dimethylamine service. This regulator has an anodized aluminum body with 316 stainless steel internal parts plus an FEP Teflon on Viton diaphragm and a Teflon seat. The delivery pressure range is 28-240 kPa (4–35 psig).

For sensitive low pressure control, Matheson low pressure regulator Model 71-240, which has an oversize pancake body of aluminum with stainless steel internal parts plus a Teflon-faced diaphragm and Teflon seat, will afford accurate low pressure control over the delivery pressure range 3.4–34.5 kPa (0.5–5.0 psig).

Manual Controls

Matheson needle valve Model 61-240, a 303 stainless steel valve, is available for direct connection to the cylinder valve outlet. It is suitable for manual flow control of the liquid or vapor phase. The valve can be equipped with a variety of outlets, such as a serrated hose end, ¼" compression fitting, or ¼" NPT male or female pipe. Needle valve Models 59 or 32S is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses

Matheson

the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Dimethylamine is classified by the DOT as a flammable, compressed gas and is shipped with the required "Red Gas Label".

Commercial Preparations

Dimethylamine is produced by the interaction of methanol and ammonia over a catalyst at high temperatures. Mono-, di-, and tri-methylamines are all produced by this process. Yields are regulated by the conditions employed.

Chemical Properties

Dimethylamine (like ammonia) dissolves in water to give an alkaline solution and forms salts with acids. Dimethylamine can react with acetic anhydride or acetyl chloride (acylation) or with benzenesulfonyl chloride (Hinsberg test) forming the corresponding substituted amide. Dimethylamine reacts with nitrous acid giving N-nitrosodimethylamine. Treating dimethylamine with esters gives N,N-dialkylamides. Dimethylamine reacts with formaldehyde giving a hydroxymethyl derivative which may react with another molecule of dimethylamine to yield bis(dimethylamino)methane. The hydroxy group in naphthols is replaceable by a dimethylamino group (Bucherer reaction). Dimethylamine reacts with carbon disulfide forming a dimethylamine salt of dimethyldithiocarbamic acid. Dimethylamine undergoes oxidation and gives a variety of products depending on the oxidizing agent used. The N-hydrogen atom is replaceable by chlorine, bromine, or iodine giving N-halodimethylamines. Dimethylamine reacts with cyanic and thiocyanic acid giving a substituted urea and thiourea, respectively. With substituted isocyanates, dimethylamine gives the unsymmetrical urea and thiourea, respectively; nitriles afford N-substituted amidines; cyanamides and substituted cyanamides yield substituted guanidines; and dicyandiamide and its substitution products yield biguanides. Dimethylamine adds to quinones and epoxides. Alkylmagnesium halides react with dimethylamine forming dimethylaminomagnesium halides and an alkane. Dimethylamine reacts readily with nonmetallic oxy- and sulfochlorides, viz, sulfur monochloride, sulfur dichloride, phosphorus trichloride, boron trichloride, etc.

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

The structural parameters calculated from microwave spectra are as follows: bond distances: C-N 1.466 Å (1.466×10^{-10} m); N-H 1.022 Å (1.022×10^{-10} m); verage C-H 1.09 Å (1.09×10^{-10} m); bond angles: C-N-C 112.2°; H-N-C 108.8°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous dimethylamine.

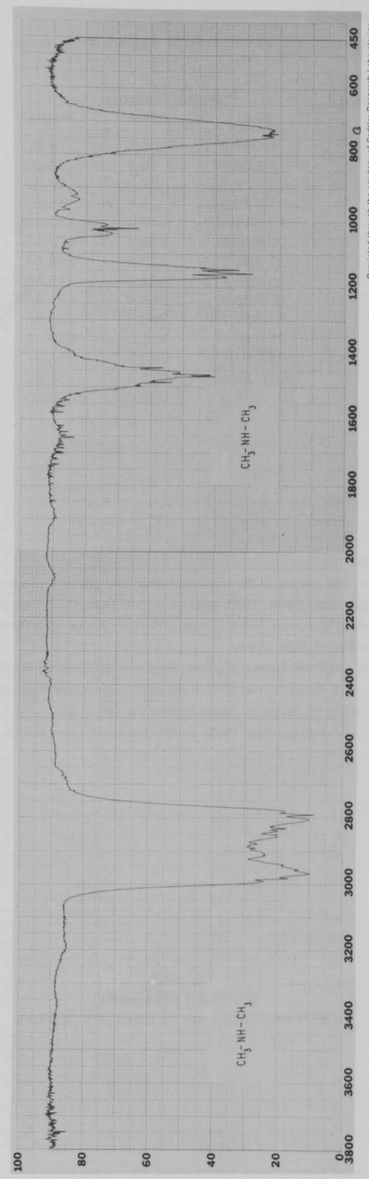


Fig. 2. Infrared specturm of gaseous dimethylamine over the frequency range 3 800-450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure: 2.666 kPa (20 mmHg) (6).

Matheson

DIMETHYLAMINE

Vapor Pressure (4)

Vapor pressure up to 101.325 kPa (1 atm) are shown below:

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
191.38	0.647 9	6.5	4.86
213.79	1.958 4	19.6	14.69
222.07	3.779 6	37.8	28.35
232.13	7.775 3	77.8	58.32
242.07	14.743 8	147.4	110.58
249.62	22.940 0	229.4	172.13
254.44	33.265 0	332.7	249.54
262.97	46.396 7	464.0	348.06
270.17	65.486 3	654.9	491.22
275.92	84.859 7	848.6	636.50
277.67	91.516 7	915.2	686.45
279.95	100.970 4	1 009.7	757.37
280.01	101.132 5	1 011.3	758.62
280.03	101.325 0	1 013.25	760.00

For vapor pressure values above 101.325 kPa, see Figure 3.

Latent Heat of Vaporization, △Hv (1)

Temperature, °K	△Hv, kJ/mol
243.15	28.67
253.15	28.11
263.15	27.53
273.15	26.92
280.03	26.50
288.15	26.40
298.15	25.30
313.15	24.23

Thermodynamic Properties of Dimethylamine As Ideal Gas @ 25 °C

Heat Capacity, C_p^o	69.036 J/(mol·°K)
Entropy, S^o	288.780 J/(mol·°K)
Enthalpy Difference, $H^o_{298} - H^o_{273}$	1.672 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of dimethylamine, see W. Braker and A. L. Mossman, **The Matheson Unabridged Gas Data Book,** *1975,* Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment,* 2nd edition, *1977,* pp. 51-55, Matheson, Lyndhurst, New Jersey.

[3] J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.* 48, 5058-5066 (1968).

[4] J. G. Aston, M. L. Eidinoff, and W. S. Forster, *J. Amer. Chem.* **Soc.** 61, 1539 (1939).

[5] K. A. Kobe and R. H. Harrison, *Petrol Refiner* 33, 161 (1954).

[6] *The Sadtler Standard Spectra, 1972,* Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Matheson

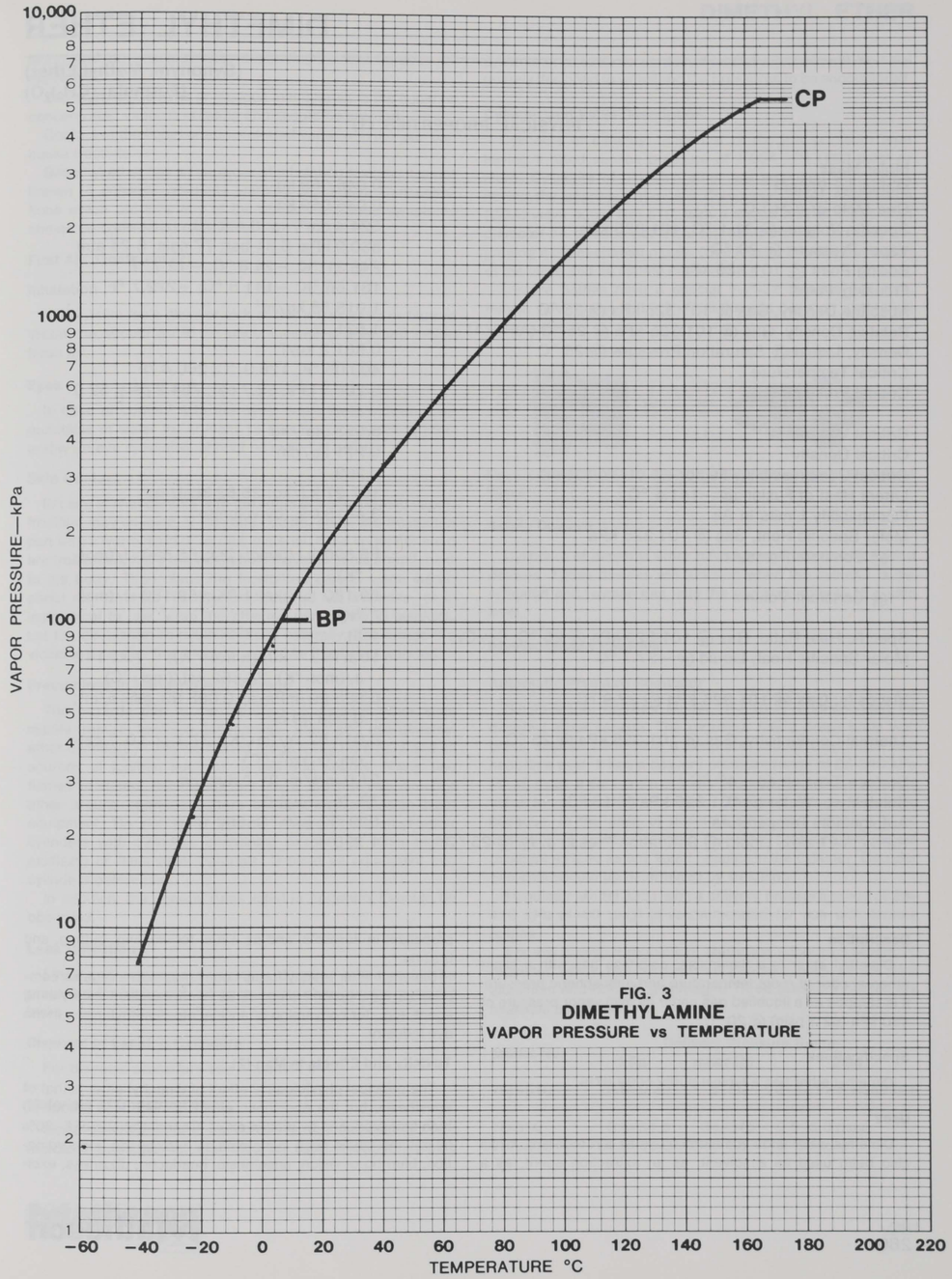


FIG. 3
DIMETHYLAMINE
VAPOR PRESSURE vs TEMPERATURE

DIMETHYL ETHER

(Synonym: Methyl Ether)
(Formula: $(CH_3)_2O$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.046 069 kg
One Mole of $(CH_3)_2O$	0.046 069 kg
Specific Volume @ 21.1 °C, 101.325 kPa	524.4 dm^3/kg; 8.4 ft^3/lb
Vapor Pressure @ 20 °C	530.9 kPa; 5.31 bar; 77 psia; 5.24 atm
Boiling Point @ 101.325 kPa	248.31 °K; −24.8 °C; −12.7 °F
Freezing Point	131.66 °K; −141.5 °C; −222.7 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	1.918 55 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.621
Density, Liquid @ Saturation Pressure @ 25 °C	0.661 2 kg/l
Critical Temperature	400.05 °K; 126.9 °C; 260.4 °F
Critical Pressure	5 268.9 kPa; 52.7 bar; 764.2 psia; 52.0 atm
Critical Volume	3.683 dm^3/kg
Critical Density	0.271 kg/dm^3
Critical Compressibility Factor	0.269
Latent Heat of Fusion @ −141.5 °C	107.27 kJ/kg; 25.62 kcal/kg
Flammability Limits In Air	3.4–18.0% (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ Constant Pressure	65.690 kJ/(kmol·°K); 65.690 J/(mol·°K);
@ Constant Volume	59.180 kJ/(kmol·°K); 59.180 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.11
Molar Specific Heat, Liquid @ −27.7 °C	103.142 kJ/(kmol·°K); 103.142 J/(mol·°K); 24.652 cal/(mol·°C)
Viscosity, Gas @ 101.325 kPa @ 22.9 °C	0.008 99 mPa·s; 0.008 99 $mN \cdot s/m^2$; 0.008 99 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.015 52 W/(m·°K); 37.1 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −40 °C	21.0 mN/m; 21.0 dyn/cm
Solubility In Water @ 101.325 kPa @ 18 °C	7% (by weight)
Autoignition Temperature	623 °K; 350 °C; 662 °F
Refractive Index, Liquid @ Saturation Pressure, n_D @ 25 °C	1.298 4

Description

Dimethyl ether is a flammable, colorless gas with a slight ethereal odor at room temperature and atmospheric pressure. It is shipped as a liquefied gas under its own vapor pressure of 430 kPa (62.3 psig) @ 20 °C.

Specifications

Dimethyl ether has a typical purity of 99.87%.

Uses

Dimethyl ether finds commercial use as a refrigerant. It has also been used as a solvent, as an extraction agent, as a propellant in aerosols, and as a fuel for welding, cutting, and brazing.

Dimethyl ether readily forms complexes with inorganic compounds, e.g., boron trifluoride. It is an excellent methylating agent, e.g., for conversion of aniline into dimethylaniline in the dye industry.

Toxicity and Effects In Man (2)

The principal physiological effect of dimethyl ether is that of anesthesia, but the anesthetic effect is much less (about ¼) than that produced by diethyl ether. Concentrations of 5–20% by volume cause such symptoms as intoxication, incoordination, blurring of vision, anesthesia, headache, dizziness, excitation and unconsciousness, depending on the duration of exposure.

Exposure of the eyes or mucous membranes to the liquid or concentrated vapor is irritating and should be avoided.

Contact of the liquid or concentrated vapor with the skin can cause frostbite.

Dimethyl ether has a low order of inhalation toxicity. It is not known to possess adequate warning properties. Concentrations which produce any of the above mentioned symptoms should be considered excessive.

First Aid Treatment (2)

Inhalation

If the victim feels dizzy or sick or has a headache or blurred vision, he should go to an uncontaminated area and inhale fresh air.

Eyes

In case of contact with the eyes, wash them with copious quantities of water for at least 15 minutes. A physician, preferably an eye specialist, should be called at once.

Skin Contact

In case of skin contact with the liquid or concentrated vapor, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The hazards due to the handling of dimethyl ether stem mainly from its extreme flammability. Store and use dimethyl ether cylinders in well-ventilated areas away from heat and all sources of ignition such as flames and sparks. Never use flames to detect flammable gas leaks. Do not use dimethyl ether around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of dimethyl ether cylinders with cylinders containing oxygen, or other highly oxidizing or flammable materials. Ground all equipment and cylinders before use.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Lines and equipment to contain dimethyl ether should be pretested for leaks with nitrogen, using soapy water to detect leaks.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-A.

Materials of Construction

Since dimethyl ether is noncorrosive, any common or commercially available material may be used. However, piping systems or vessels to contain dimethyl ether should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

Cylinders of dimethyl ether are of the low pressure type having a rated service pressure of 1 034 kPa (150 psig) or more. Cylinders of dimethyl ether are equipped with valves having the approved standard Compressed Gas Association (CGA) valve outlet No. 510, with a thread size of 0.885 inch diameter-14 threads per inch, left-hand internal threads, accepting a bullet-shaped nipple. (See Figure 1 for an illustration of the valve and its mating connection.)

Lecture bottles have a special 5/16″-32 threads per inch, female valve outlet and a 9/16″-18 threads per inch, male dual valve outlet.

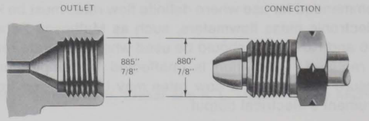


Fig. 1. CONNECTION 510 .885″-14 LH INT. accepting a Bullet Shaped Nipple

Safety Devices

Cylinders of dimethyl ether have spring-loaded safety relief devices. These devices will function when the cylinder is overheated and release gas until the pressure returns to a safe level.

Recommended Controls

Automatic Pressure Regulator

Single stage regulator Model 1P-510 is recommended for dimethyl ether service. The regulator has a brass body with brass internal parts plus a neoprene rubber diaphragm and neoprene seat. It has a delivery pressure range of 28-240 kPa (4–35 psig). It contains a delivery pressure gauge and a needle valve for accurate flow control. The tank gauge is omitted because, in the case of dimethyl ether, the pressure is no indication of cylinder content; the vapor pressure will remain constant as long as any liquid remains in the cylinder. Cylinder contents should be determined by weighing.

Regulator Model 3321 with a delivery pressure range of 28–410 kPa (4–60 psig) is recommended for use with lecture bottles.

For low pressure regulation, Matheson supplies a Model 70 regulator which has an oversize pancake body of die cast aluminum and Buna N diaphragm. Three pressure ranges are available as follows:

Model No.	Delivery Pressure Range		
	kPa	mbar (g)	psig
70B-510	0.5–0.30	5–30	2–12 inch water column
70-510	3.4–34.5	34–345	0.5–5.0 psig
70A-510	34.5–68.9	345–689	5–10 psig

Manual Controls

Matheson manual needle Model 50-510, a brass bar stock valve, is available for direct connection to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, ¼" compression fitting, or ¼" NPT male or female pipe. This valve is used mainly for intermittent flow control but this requires close supervision. It should not be used as a pressure control since dangerous pressures may develop if a system or line becomes plugged. A Model 31B needle valve is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Dimethyl ether is classified by the DOT as a flammable, compressed gas and is shipped under the required "Red Gas Label".

Commercial Preparation

Dimethyl ether is prepared by the dehydration of methanol with sulfuric acid or by dehydration over alumina at high pressures and temperatures.

Chemical Properties

Dimethyl ether is not attacked by boiling alkalis. Halogenation gives a series of halogen substituted ethers. Dimethyl ether is cleaved by hydriodic acid at temperatures of 100 °C. At low temperatures, dimethyl ether forms a series of addition compounds with the halogens and halogen hydrides. It forms an addition compound with boron trifluoride. Dimethyl ether reacts with oleum to give dimethyl sulfate. It can be oxidized catalytically to formaldehyde.

Dimethyl ether reacts with carbon monoxide to give acetic anhydride and (or) methyl acetate. It reacts with acetic acid to give methyl acetate. It reacts with phthalic anhydride to give dimethyl phthalate. It methylates phenol to give anisole. Dimethyl ether reacts with hydrogen cyanide to form acetonitrile.

Thermodynamic and Detailed Physical Data

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous dimethyl ether.

Vapor Pressure (3)

Vapor pressure data below 101.325 kPa (1 atm) are shown below. The values have been calculated by the following Antoine vapor pressure equation:

$$\log_{10} p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constant A, B, and C have the values of 7.316 46, 1 025.56, and 256.05, respectively.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
179.45	1.333	13.3	10
187.55	2.666	26.7	20
196.55	5.333	53.3	40
203.28	7.999	80.0	60
206.55	10.659	106.6	80
210.01	13.324	133.3	100
221.59	26.659	266.6	200
229.13	39.993	400.0	300
234.64	53.327	533.3	400
239.21	66.652	666.6	500
243.08	79.986	799.9	600
246.47	93.320	933.2	700
248.31	101.325	1 013.25	760

Vapor pressure data above 101.325 kPa (1 atm) are listed below (4).

Temperature, °K	Vapor Pressure kPa	bar	atm
273.15	255.339	2.55	2.52
282.40	362.744	3.63	3.58
289.95	464.069	4.64	4.58
296.90	571.473	5.71	5.64
306.70	758.924	7.59	7.49
319.28	1 044.661	10.4	10.31
329.17	1 328.371	13.3	13.11
337.83	1 616.134	16.2	15.95
353.25	2 243.336	22.4	22.14
363.40	2 715.510	27.2	26.80
373.05	3 256.586	32.6	32.14
383.72	3 933.437	39.3	38.82
389.97	4 398.518	44.0	43.41
395.35	4 830.163	48.3	47.67
400.05 (C.T.)	5 268.900	52.7	52.00 (C.P.)

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv (1)

Temperature, °K	ΔHv, kJ/kg
203.15	516.146
223.15	494.660
243.15	475.508
248.31	467.100
253.15	461.029
273.15	436.037
293.15	411.935
313.15	377.510
333.15	342.384

Thermodynamic Properties of Dimethyl Ether As Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	64.392 J/(mol·°K); 15.39 cal/(mol·°K)
Entropy, S°	266.270 J/(mol·°K); 63.64 cal/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	14.083 kJ/mol; 3.366 kcal/mol
Enthalpy of Formation, ΔH_f°	−184.054 kJ/mol; −43.99 kcal/mol
Gibbs Energy of Formation, ΔG_f°	−112.675 kJ/mol; −26.93 kcal/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of dimethyl ether, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 7–11, Matheson, Lyndhurst, New Jersey.

[3] B. J. Zwolinski, *et al.*, **Selected Values of Properties of Chemical Compounds**, *1968*, Volume 1, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[4] E. Cardosa and A. Bruno, *J. Chem. Phys.* 20, 347 (1963).

[5] D. D. Wagman, *et al.*, *Selected Values of Chemical Thermodynamic Properties*, *1968*, p. 140, Natl. Bur. Stand. Tech. Note 270-3, U. S. Government Printing Office, Washington, D. C.

[6] *The Sadtler Standard Spectra*, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

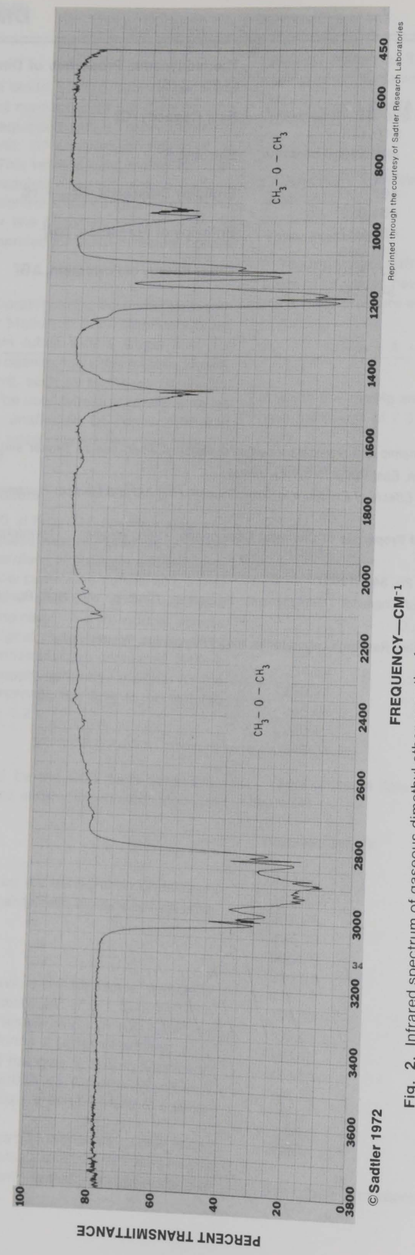


Fig. 2. Infrared spectrum of gaseous dimethyl ether over the frequency range 3 800-450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure: 4.00 kPa (30 mmHg) (6).

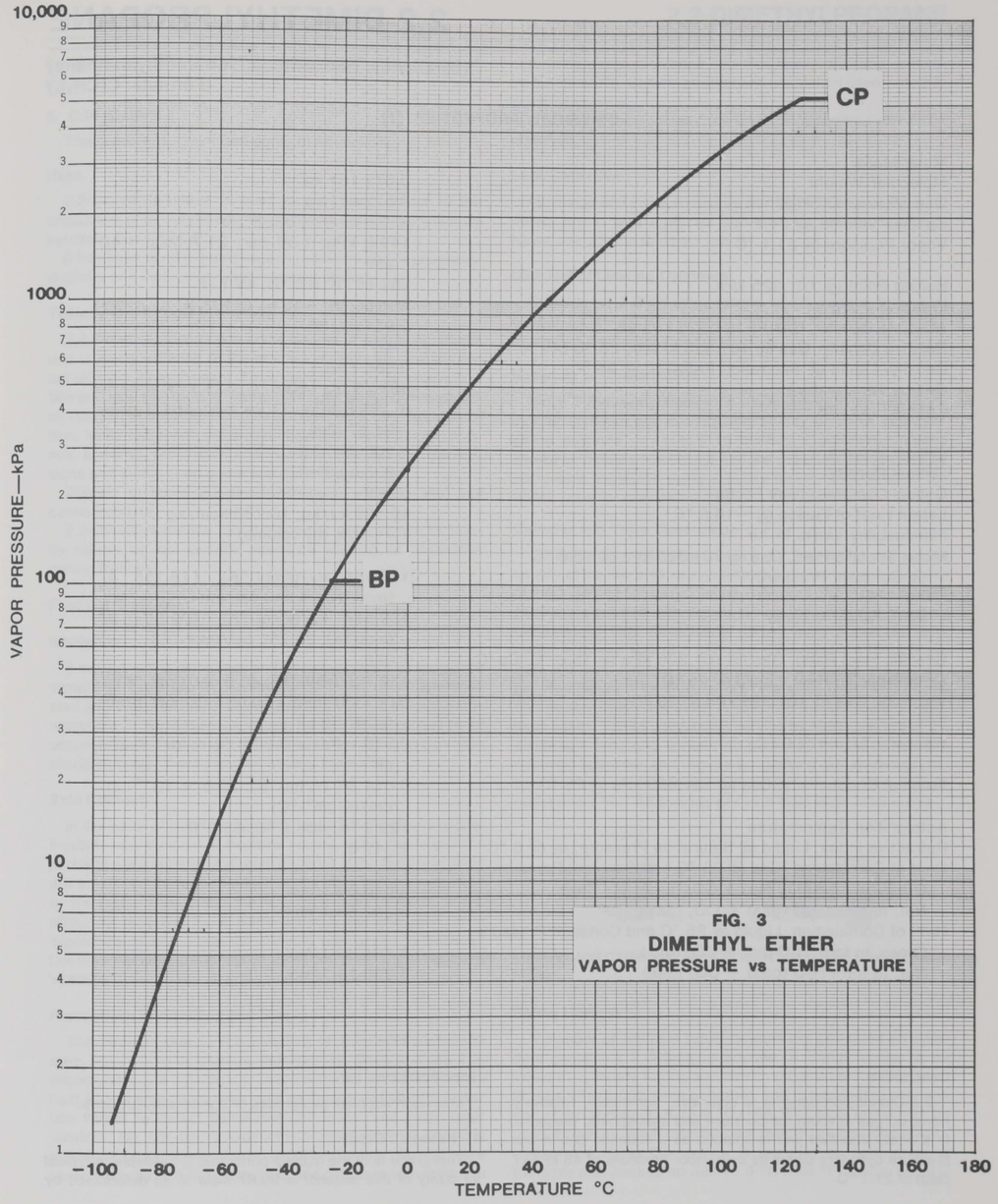


FIG. 3
DIMETHYL ETHER
VAPOR PRESSURE vs TEMPERATURE

2,2-DIMETHYLPROPANE

(Synonyms: Neopentane; Tetramethylmethane)
(Formula: $C(CH_3)_4$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.072 151 kg
One Mole of $C(CH_3)_4$	0.072 151 kg
Specific Volume @ 21.1 °C, 101.325 kPa	330.8 dm^3/kg 5.3 ft^3/lb
Vapor Pressure @ 21.1 °C	149.6 kPa; 1.50 bar; 21.7 psia; 1.48 atm
Boiling Point @ 101.325 kPa	282.65 °K; 9.5 °C; 49.1 °F
Freezing Point	256.60 °K; −16.6 °C; 2.2 °F
Absolute Density, Gas @ 101.325 kPa 25 °C	2.951 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	2.49
Density, Liquid @ Saturation Pressure @ 25 °C	0.585 1 kg/l
Critical Temperature	433.75 °K; 160.6 °C; 321.1 °F
Critical Pressure	3 198.8 kPa; 31.99 bar; 464.0 psia; 31.57 atm
Critical Volume	4.200 dm^3/kg
Critical Density	0.238 kg/dm^3
Critical Compressibility Factor	0.269
Latent Heat of Fusion @ −16.6 °C	45.129 kJ/kg; 10.786 kcal/kg
Flammability Limits In Air	1.4–7.5% (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ 15.6 °C	
@ Constant Pressure	118.156 kJ/(kmol·°K); 118.156 J/(mol·°K) 28.240 cal/(mol·°C)
@ Constant Volume	109.854 kJ/(kmol·°K); 109.854 J/(mol·°K); 26.256 cal/(mol·°C)
Specific Heat Ratio, Gas @ 101.325 kPa @ 15.6 °C, Cp/Cv	1.076
Molar Specific Heat, Liquid @ 25 °C	170.7 J/(mol·°K); 40.8 cal/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.007 00 mPa·s; 0.007 00 mN·s/m^2; 0.007 00 cP
Viscosity, Liquid @ 0 °C	0.328 mPa·s; 0.328 mN·s/m^2; 0.328 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.014 86 W/(m·°K); 35.5 × 10^{-6} cal·cm/(s·cm^2·°C)
Autoignition Temperature	729.3 °K; 456.2 °C; 853 °F
Refractive Index, Liquid (@ Saturation Pressure, n_D @ 6 °C	1.347 6
Heat of Combustion, Gas @ 25 °C and Constant Pressure	
Gross, to form H_2O (liq) + CO_2 (gas)	3 516.6 kJ/mol
Net, to form H_2O (gas) + CO_2 (gas)	3 252.5 kJ/mol
Heat of Combustion, Liquid @ 25 °C and Constant Pressure	
Gross, to form H_2O (liq) + CO_2 (gas)	3 494.3 kJ/mol
Net, to form H_2O (gas) + CO_2 (gas)	3 230.1 kJ/mol

Description

2,2-Dimethylpropane is a colorless, flammable, relatively nontoxic gas at room temperature and atmospheric pressure. It is easily liquefied and is shipped as a liquefied gas in low pressure cylinders under its own vapor pressure of 48 kPa (7 psig) at 21.1 °C.

Specifications

Matheson supplies two grades of 2,2-dimethylpropane.

1. Research Grade

This grade is of the highest purity that is available. A typical lot purity of this material is 99.87 mole % as determined by freezing point. This material is supplied with a statement of purity.

2. C.P. Grade

This grade has a minimum purity of 99 mole %.

Uses

2,2-Dimethylpropane is used as the raw material in the production of isobutylene, which in turn is used to manufacture synthetic Butyl rubber.

It has been used in halogenation reactions and in photoconductivity and molecular rearrangement studies.

Toxicity and Effects In Man (2)

2,2-Dimethylpropane has some degree of anesthetic action and is mildly irritating to the mucous membranes and/or can act as a simple asphyxiant. Thus, depending on the concentration and time of exposure, symptoms such as rapid respiration, air hunger, diminished mental alertness, muscular incoordination, faulty judgment, emotional instability, rapid fatigue, nausea, vomiting, prostration and loss of consciousness, convulsions and finally deep coma and death may occur.

Contact of liquid 2,2-dimethylpropane with the skin can cause frostbite.

2,2-Dimethylpropane has a low order of inhalation toxicity. Its vapors do not provide adequate warning of hazardous concentrations.

First Aid Treatment

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration and oxygen simultaneously. Treat symptomatically thereafter.

Skin Contact

In the case of skin contact with liquid 2,2-dimethylpropane, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The hazards due to the handling of 2,2-dimethylpropane stem mainly from its extreme flammability. Store and use 2,2-dimethylpropane cylinders in well-ventilated areas away from heat and all ignition sources such as flames and sparks. Never use flames to detect flammable gas leaks, use soap water solution. Do not use 2,2-dimethylpropane around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of 2,2-dimethylpropane cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all lines and equipment used with 2,2-dimethylpropane.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

All fittings and joints should be painted with soap solution to detect leaks, which will be indicated by bubble formation. Never use a flame to detect leaks.

Disposal of Leaking Cylinders

Cylinders of 2,2-dimethylpropane which develop leaks that cannot be corrected normally may be disposed of by the procedure described in Appendix II-A.

Materials of Construction

Since 2,2-dimethylpropane is a noncorrosive gas any common or commercially available metal may be used. However, piping systems or vessels to contain 2,2-dimethylpropane should be designed to have a working pressure as specified by competent engineers using a safety factor conforming to the ASME code for pressure piping.

Cylinder and Valve Description

DOT approved cylinders containing 2,2-dimethylpropane are usually of the low pressure type having a rated service pressure of 1 034 kPa (150 psig) or more. Cylinders of 2,2-dimethylpropane are equipped with valves having the approved standard Compressed Gas Association (CGA) valve outlet No. 510, having a thread size of 0.885 inch diameter—14 threads per inch, left-hand internal threads accepting a bullet-shaped nipple. See Figure 1 for illustration of the valve outlet and mating connection. This valve outlet is standard for all liquefied petroleum gases. Valves used in this service by Matheson are of the diaphragm type and contain no packing. They are therefore relatively leak-free and require no packing adjustments. Lecture bottles have a special 5/16"-32 threads per inch, female outlet and a 9/16"-18 threads per inch male dual valve outlet.

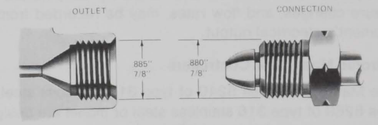


Fig. 1. CONNECTION 510 .885"-14 LH INT. accepting a Bullet Shaped Nipple

Safety Devices

A number of different safety devices are permitted on cylinders containing 2,2-dimethylpropane. A frangible disc is allowed in cylinders having a minimum required test pressure of 20 684 kPa (3 000 psig) or higher, and is required in only one end of the container. A 73.9 °C (165 °F) fusible metal may be used. However, when cylinders are over 30 inches long (exclusive of the neck) this device is required on both ends. A frangible disc backed up with 73.9 °C (165 °F) fusible metal is

permitted in cylinders having a minimum required test pressure of 20 684 kPa (3 000 psig) or higher; when cylinders are over 30 inches long (exclusive of the neck) this device is required at both ends. The most commonly used safety device, which is employed by Matheson, is the spring-loaded safety relief valve. If cylinder pressure becomes dangerously high, usually due to overheating, the safety relief device will open (at approximately 2 586 kPa (375 psig) and release 2,2-dimethylpropane gas until the pressure again returns to a safe level.

Recommended Controls

Manual Valves

Matheson needle valve Model 50-510, a brass bar stock valve, is available for direct connection to the cylinder valve outlet. It can be equipped with a variety of outlets. When the pressure of 2,2-dimethylpropane is raised by the controlled application of heat (no greater than 51.7 °C (125 °F)), it is suggested that a Model 70 low pressure regulator be used to reduce and control pressure at a constant value. Matheson Model 70 regulator is available with 3 delivery pressure ranges as follows:

Model No.	Delivery Pressure Range		
	kPa	mbar (g)	psig
70B-510	0.5–3.0	5–30	2–12 inch water column
70-510	3.4–34.5	34–345	0.5–5.0 psig
70A-510	34.5–68.9	345–689	5–10 psig

A Model 31B needle valve is recommended for use with lecture bottles.

Flowmeters

Metheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates, may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

2,2-Dimethylpropane is classified by the DOT as a flammable liquid requiring a "Red Label".

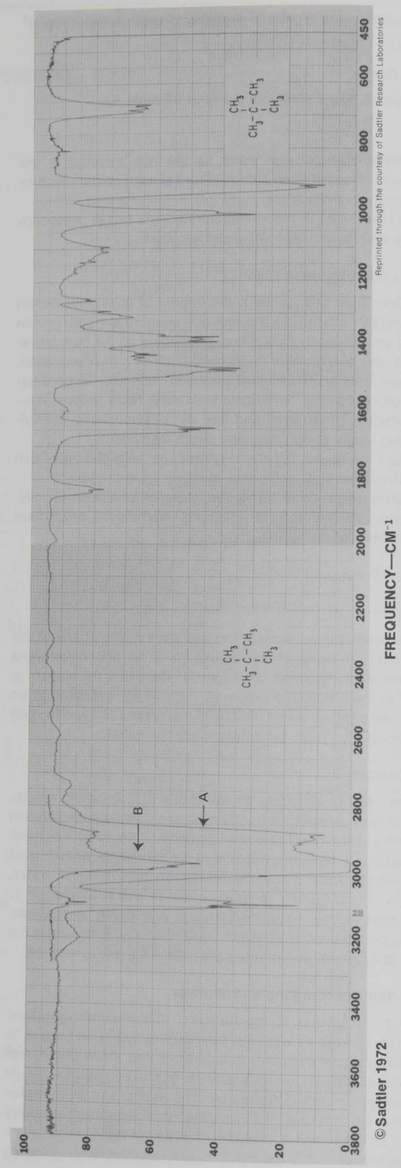


Fig. 2. Infrared spectrum of gaseous 2,2-dimethylpropane over the frequency range 3 800–450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure: curve A (complete scan): 6.666 kPa (50 mmHg); curve B (partial scan): 0.667 kPa (5.0 mmHg) (8).

Commercial Preparation

2,2-Dimethylpropane has been prepared synthetically by a number of different methods, but the present relatively small commercial quantities are obtained by fractionation of the liquid hydrocarbon mixtures recovered after separation of butanes from natural gas.

Chemical Properties

2,2-Dimethylpropane is a branched chain hydrocarbon of the alkane family and it undergoes the reactions typical of this group of hydrocarbons.

Thermodynamic and Detailed Physical Data

Infrared Spectrum

See Figure 2 for the infrared spectrum of 2,2-dimethylpropane.

Vapor Pressure

Vapor pressure values between 213.15 °K and 328.15 °K have been calculated by the following Antoine vapor pressure equation (3):

$$\log_{10} p = A - \frac{B}{C + T}$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.738 12, 950.84, and 237.0, respectively. Some calculated vapor pressure values are shown below:

Temperature, °K	Vapor Pressure		
	kPa	bar	mmHg
213.15	3.093	0.031	23.2
233.15	10.879	0.109	81.6
253.15	30.290	0.303	227.2
273.15	70.967	0.710	532.3
282.653	101.325	1.013 25	760.0
293.15	145.640	1.456	1 092
313.15	210.449	2.104	1 578
328.15	404.366	4.044	3 033

Vapor pressures between 323.15 °K and 433.75 °K (critical temperature) are shown below (4):

Temperature, °K	Vapor Pressure		
	kPa	bar	atm
323.15	355.549	3.56	3.509
330.15	426.984	4.27	4.214
348.15	658.005	6.58	6.494
373.15	1 117.919	11.2	11.033
398.15	1 779.774	17.8	17.565
423.15	2 702.642	27.0	26.673
431.15	3 069.540	30.7	30.294
433.75	3 199.033	32.0	31.572

For additional data, see Table 1.
See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv (1)

Temperature, °K	ΔHv, kJ/kg
213.15	364.080
233.15	350.992
253.15	337.432
273.15	322.926
282.65	315.357 (5)
298.15	301.845 (5)

Thermodynamic Data

See Table 1 for the thermodynamic properties of saturated 2,2-dimethylpropane, and Table 2 for the thermodynamic properties of gaseous 2,2-dimethylpropane.

Thermodynamic Properties of 2,2-Dimethylpropane As Ideal Gas @ 25 °C (5) (6)

Heat Capacity, C_p°	243.174 J/(mol·°K)
Enthalpy, H°	2.931 kJ/mol
Enthalpy of Formation, ΔH_f°	−166.0 kJ/mol
Free Energy of Formation, ΔF_f°	−15.23 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of 2,2-dimethylpropane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, 1975, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, 1977, pp. 11–16, Matheson, Lyndhurst, New Jersey.

[3] R. R. Dreisbach, *Physical Properties of Chemical Compounds*, 1959, Volume 2, p. 18, Adv. in Chem. Ser. No. 22, American Chemical Society, Washington, D. C.

[4] J. A. Beattie, D. R. Douslin, and S. W. Levine, *J. Chem. Phys.* 19, 948 (1951).

[5] C. E. Miller and F. D. Rossini, *Physical Constants of Hydrocarbons, C_1 to C_{10}, 1961*, American Petroleum Institute, New York, New York.

[6] K. A. Kobe and R. Pennington, *Petrol. Refiner.* 29, 93 (1950).

[7] P. P. Dawson, Jr., J. J. McKetta, and I. H. Silverberg, *J. Chem. Eng. Data* 18, 76–78 (1973).

[8] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED NEOPENTANE (7)

Temperature		Pressure		Entropy J/(kg•K)		Enthalpy kJ/kg		Latent Heat of Vaporization kJ/kg	Specific Volume m^3/kg		Density kg/m^3	
°K	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
344.44	160.33	604.050	5.962	0.000	762.743	0.000	262.802	262.802	0.001 90	0.054	526.3	18.52
352.78	175.33	729.879	7.203	71.965	779.898	25.197	274.935	249.738	0.001 94	0.046	515.5	21.74
361.11	190.33	873.979	8.626	134.306	796.634	47.791	286.953	239.162	0.001 99	0.038	502.5	26.32
369.44	205.33	1 037.80	10.24	197.066	813.788	71.105	298.970	227.865	0.002 04	0.032	490.2	31.25
377.78	220.33	1 223.20	12.07	259.826	830.942	95.000	310.732	215.732	0.002 10	0.026	476.2	38.46
386.11	235.33	1 432.04	14.13	323.005	847.678	119.639	322.145	202.506	0.002 17	0.022	460.8	45.45
394.44	250.33	1 666.46	16.45	386.602	862.741	144.999	332.814	187.815	0.002 25	0.018	444.4	55.56
402.78	265.33	1 927.70	19.02	451.035	876.130	171.265	342.414	171.149	0.002 35	0.015	425.5	66.67
411.11	280.33	2 219.35	21.90	518.816	887.426	199.577	351.084	151.507	0.002 48	0.012	403.2	83.33
419.44	295.33	2 544.72	25.11	590.362	892.447	229.980	356.732	126.752	0.002 66	0.009 9	375.9	101.01
427.78	310.33	2 907.52	28.70	677.808	888.682	268.032	358.313	90.281	0.002 97	0.007 5	336.7	133.33
433.33	320.33	3 172.48	31.31	802.073	876.130	322.679	354.687	32.008	0.003 65	0.005 3	274.0	188.68

Table 2. THERMODYNAMIC PROPERTIES OF GASEOUS NEOPENTANE AT 344.44°K (620 °R) (7)

P, Pressure, kPa; **H**, Enthalpy, kJ/kg; **S**, Entropy, J/(kg·°K); **V**, Specific Volume, m^3/kg

P	H	S	V
34.474	281.49	1 131.772	1.142 4
68.948	280.56	1 049.766	0.566 8
103.421	279.63	1 001.231	0.374 8
137.895	278.47	966.086	0.278 8
172.369	277.54	938.053	0.221 2
206.843	276.38	915.041	0.182 7
241.317	275.45	894.958	0.155 2
275.790	274.28	877.385	0.134 6
344.738	272.19	847.260	0.105 6
413.685	269.87	821.319	0.086 3
482.633	267.54	798.726	0.072 4
551.581	264.99	778.224	0.061 8

Matheson

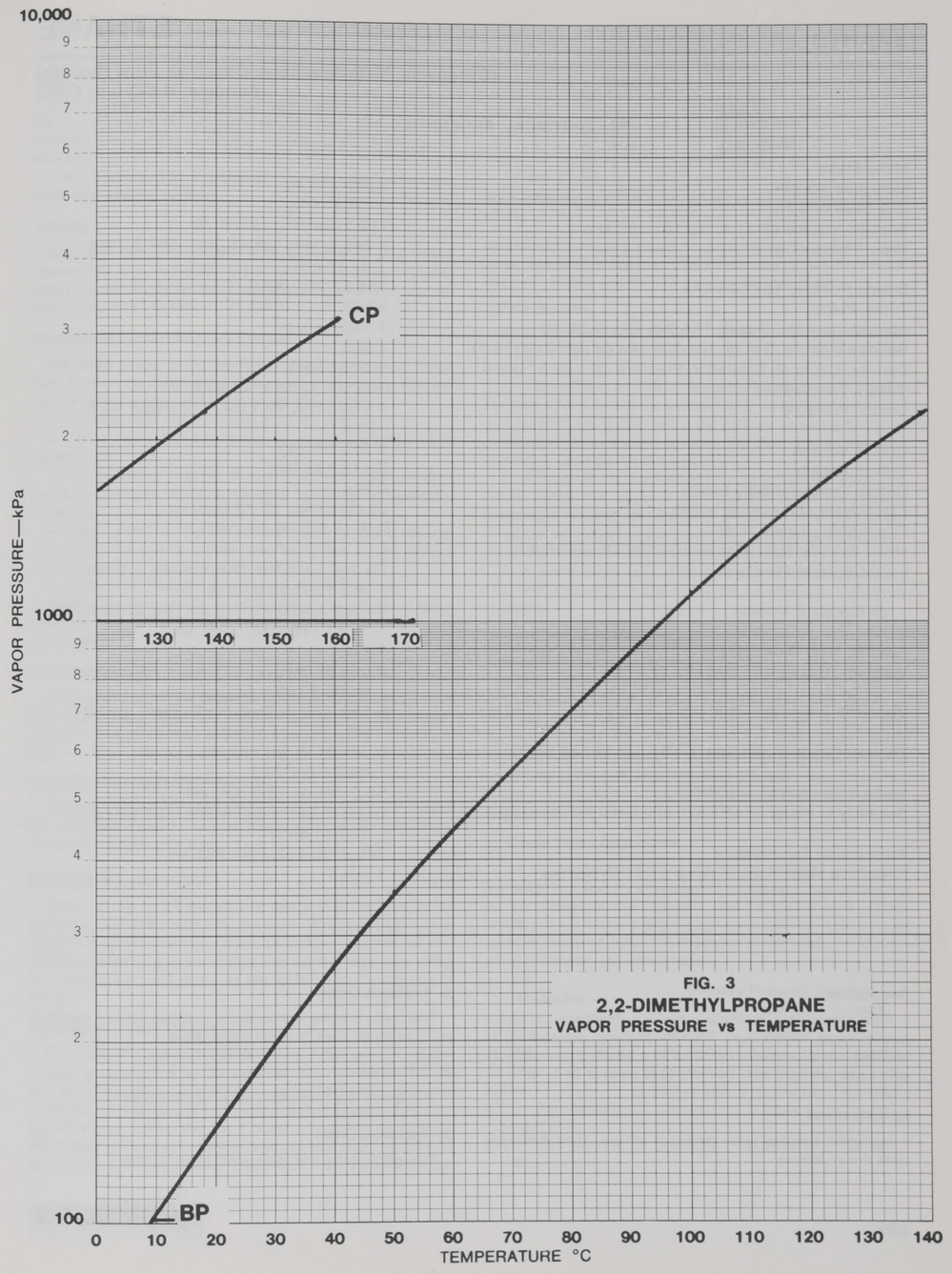


FIG. 3
2,2-DIMETHYLPROPANE
VAPOR PRESSURE vs TEMPERATURE

ETHANE

(Synonyms: Methylmethane; Dimethyl; Ethyl Hydride)
(Formula: H_3CCH_3 or C_2H_6)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.030 070 kg
One Mole of C_2H_6	0.030 070 kg
Specific Volume @ 21.1 °C, 101.325 kPa	799.1 dm^3/kg; 12.8 ft^3/lb
Vapor Pressure @ 21.1 °C	3 845.2 kPa; 38.45 bar; 557.7 psia; 37.95 atm
Boiling Point @ 101.325 kPa	184.52 °K; −88.6 °C; −127.5 °F
Triple Point	89.88 °K; −183.3 °C; −297.9 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	1.242 0 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.048
Density, Liquid @ Saturation Pressure @ −88.6 °C	0.546 5 kg/l
Critical Temperature	305.50 °K; 32.4 °C; 90.2 °F
Critical Pressure	4 914.3 kPa; 49.1 bar; 712.8 psia; 48.5 atm
Critical Volume	4.713 dm^3/kg
Critical Density	0.212 2 kg/dm^3
Critical Compressibility Factor	0.274
Latent Heat of Fusion @ −183.3 °C	95.09 kJ/kg; 22.73 kcal/kg
Flammability Limits In Air	3.0–12.5% (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ 26.8 °C	
@ Constant Pressure	53.346 kJ/(kmol·°K); 53.346 J/(mol·°K); 12.750 cal/(mol·°C)
@ Constant Volume	44.769 kJ/(kmol·°K); 44.769 J/(mol·°K); 10.700 cal/(mol·°C)
Specific Heat Ratio, Gas @ 101.325 kPa @ 26.8 °C, Cp/Cv	1.192
Viscosity, Gas @ 101.325 kPa @ 0 °C	0.008 52 mPa·s; 0.008 52 $mN·s/m^2$; 0.008 52 cP
Viscosity, Liquid @ −100 °C	0.192 mPa·s; 0.192 $mN·s/m^2$; 0.192 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.021 01 W/(m·°K); 48.1 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −100 °C	18.0 mN/m; 18.0 dyn/cm
Solubility In Water @ 101.325 kPa (total pressure) @ 0 °C	0.098 2 cm^3/1 cm^3 water; 0.013 2 kg/100 kg water
Autoignition Temperature	745.4 °K; 472.2 °C; 882 °F
Refractive Index, Liquid, n_D @ 37.9 °C, 6.9 bar	1.004 7

Description

Pure ethane is a colorless, odorless, flammable, nontoxic gas at room temperature and atmospheric pressure. It is shipped in high pressure cylinders as a liquefied gas under its own vapor pressure of 3 744 kPa (543 psig) at 21.1 °C.

Specifications

Matheson supplies three grades of ethane. Their specifications are as follows:

1. **Research Grade**

This grade is of the highest purity available. It has a minimum purity of 99.96 mole % in the liquid phase.

2. **C.P. Grade**

This grade has a minimum purity of 99.0 mole %.

3. **Technical Grade**

This grade has a minimum purity of 95.0 mole %.

Uses

Ethane possesses marked antiknock qualities which permits the use of motors of high compression ratios. It is commonly used as a raw material for the manufacture of halogenated ethanes.

It has been used as a refrigerant for extremely low temperature refrigerating systems.

Toxicity

Ethane is not considered a toxic gas. It acts as a simple asphyxiant, and in higher concentrations its action is anesthetic. No definite symptoms have been observed in concentrations up to 5%.

Precautions in Handling and Storage

The major hazard in the handling and storing of ethane stems from its extreme flammability. Therefore, the following precautions should be observed when handling this gas:

1. Keep ignition sources away from the cylinder.
2. Never use a flame to detect flammable gas leaks—use soapy water.
3. Do not store reserve stocks of ethane with cylinders containing oxygen, chlorine, or other oxidizing or flammable materials.
4. Never store cylinders of ethane in an area where leakage can cause the gas to diffuse and be ignited by an ignition source such as a spark from a motor.
5. Ground all lines and equipment used with ethane.

Aside from these specific precautions to be observed when handling ethane, the general rules listed in Appendix I should be observed.

Leak Detection

Connections or piping suspected of leaks should be painted with soapy water. Bubbling will indicate the point of leakage. Under no circumstances should a flame be used to detect a leak.

Disposal of Leaking Cylinders

Cylinders containing ethane which develop leaks that cannot be corrected normally may be disposed of by the procedure described in Appendix II-A.

Materials of Construction

Since ethane is a noncorrosive gas any common or commercially available metal may be used. However, piping systems or vessels to contain ethane should be designed to have a working pressure as specified by competent engineers using a safety factor conforming to the ASME code for pressure piping.

Cylinder and Valve Description

The approved standard cylinder valve outlet used in ethane service is designated as Compressed Gas Association (CGA) No. 350. The valve outlet thread size is 0.825 inch diameter left-hand, 14 threads per inch, with external threads accepting a ball-shaped nipple. The valve outlet and mating connection are shown in Figure 1. Valves used by Matheson for ethane service are of the packless diaphragm type eliminating the problem of leakage through packing. A special valve is used on lecture bottles and the outlet thread size is 5/16"-32 threads per inch, female and 9/16"-18 threads per inch male.

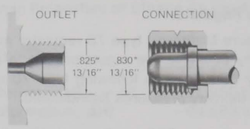


Fig. 1. CONNECTION 350 .825"-14 LH EXT. accepting Round Shaped Nipple

Safety Devices

Safety devices used on DOT approved cylinders and approved by the Bureau of Explosives for ethane are as follows:

1. A frangible disc. This is incorporated into the valve and is required in one end of the cylinder only. With this device total gas contents are discharged if the cylinder pressure becomes dangerously high enough to burst the disc. This is the most commonly used device in service.
2. A frangible disc backed up by a 73.9 °C (165 °F) melting fusible metal. This device is permitted only in cylinders having a minimum required test pressure of 20 684 kPa (3000 psig) or higher; when cylinders are over 30 inches long (exclusive of the neck) this device is required at both ends.
3. A safety relief valve. This device is of the spring-loaded type and is required in one end of the cylinder only regardless of length.

Recommended Controls

Automatic Pressure Regulators

The regulators recommended for use with ethane apply to all three grades of ethane (with the exception of the Model 2-350 regulator, which is recommended only for the C.P. and Technical Grades. Since Research Purity Grade ethane is not supplied in lecture bottles, the lecture bottle controls indicated apply only to the C.P. and Technical Grades.

The following types of automatic regulators are available for use with ethane:

1. Single Stage Regulators

The single stage regulator will reduce cylinder pressure in one stage to a delivery pressure in a particular range depending on the design of the regulator and its spring load. These regulators will show a slight variation in delivery pressure as cylinder pressure falls. The following single stage regulators are available for use with ethane:

Model No.	Delivery Pressure Range kPa	bar (g)	psig
1P-350	28–240	0.28–2.4	4–35
1L-350	28–550	0.28–5.5	4–80
1H-350	69–1 240	0.69–12.4	10–180
2-350	340–4 480	3.4–44.8	50–650
3320 (for lecture bottles only)	28–410	0.28–4.1	4–60
3321 (for lecture bottles only)	28–410	0.28–4.1	4–60

Low Pressure Regulator

A low pressure Matheson type 70 regulator may be used in series with any of the above regulators set to a pressure of approximately 50 psig. The following type 70 regulators are available with delivery pressures as indicated.

Model No.	Delivery Pressure Range kPa	mbar (g)	psig
70B	0.5–3.0	5–30	2–12 inches water column
70	3.4–34.5	34–345	0.5–5.0 psig
70A	34.5–69	345–690	5–10 psig

2. Two Stage Regulators

These regulators will show no change in delivery pressure as cylinder pressure falls. Since ethane is a liquefied gas and the vapor pressure will remain constant until the liquid phase disappears, no real advantage may be gained in using a double stage regulator, except that greater service life may be expected, and delivery pressure may be maintained constant when the liquid phase has been dissipated. Also, ethane will convert completely to a gas above its critical temperature of 32.2 °C (90 °F) in which case a two stage regulator will provide greater accuracy in delivery pressure as the cylinder pressure falls under these conditions. Matheson two stage regulators recommended for ethane are as follows:

Model No.	Delivery Pressure Range kPa	bar (g)	psig
8L-350	14–104	0.14–1.04	2–15
8-350	28–340	0.28–3.4	4–50
8H-350	69–690	0.69–6.9	10–100
9-350	138–1720	1.38–17.2	20–250

Manual Controls

Manual flow controls are available in the form of needle valves to attach directly to the cylinder valve outlet. Matheson needle valve Model 50-350 or needle valve Model 52-350 with tank gauge may be used for all cylinder sizes except lecture bottles. These valves may be equipped with a variety of outlets, such as a serrated hose end, ¼" compression fitting, or ¼" NPT male or female pipe. Models 30 AR and 31B are available for direct attachment to lecture bottles. Needle valves are recommended for manual flow control but require constant supervision. They should not be used as pressure controls since dangerous pressures may develop if a line or system becomes plugged.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Ethane is shipped as a flammable compressed gas, taking a "Red Gas Label".

Commercial Preparation

Ethane is obtained as a petroleum product from the cracking of light petroleum fractions.

Chemical Properties

Ethane is a relatively inert saturated hydrocarbon. It is of minor importance chemically. None of the C—H or C—C bonds are attacked at ordinary temperatures by sulfuric acid or by an oxidizing agent such as bromine (in the dark), oxygen, or potassium permanganate. Ethane is similarly stable under ordinary conditions to reducing agents such as hydrogen in the presence of such catalysts as platinum, palladium or nickel. It can be chlorinated under appropriate conditions to give ethyl chloride. Ethane is attacked by oxygen at elevated temperatures and, if oxygen is in excess, complete combustion occurs to carbon dioxide and water.

The conversion of ethane to ethylene is highly endothermic and requires a greater heat input than cracking propane.

Thermodynamic Data

The thermodynamic properties of saturated ethane, superheated vapor, and compressibility data are shown in Tables 1, 2 and 3, respectively.

Thermodynamic and Detailed Physical Data

Molecular Structure

Ethane has D_{3d} symmetry, a symmetry number of six, and the following bond distances and angle: C—H 1.09 Å (1.09 × 10^{-10} m); C—C 1.55 Å (1.55 × 10^{-10} m); H—C—H 109.5° (1).

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous ethane.

Vapor Pressure (2)

@ −88.6 °C	101.325 kPa
@ 32.4 °C	4 914 kPa

For additional vapor pressure data, see Table 1 and Figure 3.

Latent Heat of Vaporization, ΔHv

@ −88.6 °C	14.715 kJ/mol; 489.4 kJ/kg; 3 517.0 cal/mol

For additional ΔHv data, see Table 1.

Thermodynamic Properties of Ethane As Ideal Gas @ 25 °C (3)

Heat Capacity, C_p°	52.635 J/(mol·°K)
Entropy, S°	229.492 J/(mol·°K)
Enthalpy Difference, $H^\circ_{298} - H^\circ_0$	11.950 kJ/mol
Enthalpy of Formation, ΔH_f°	−84.683 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of ethane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

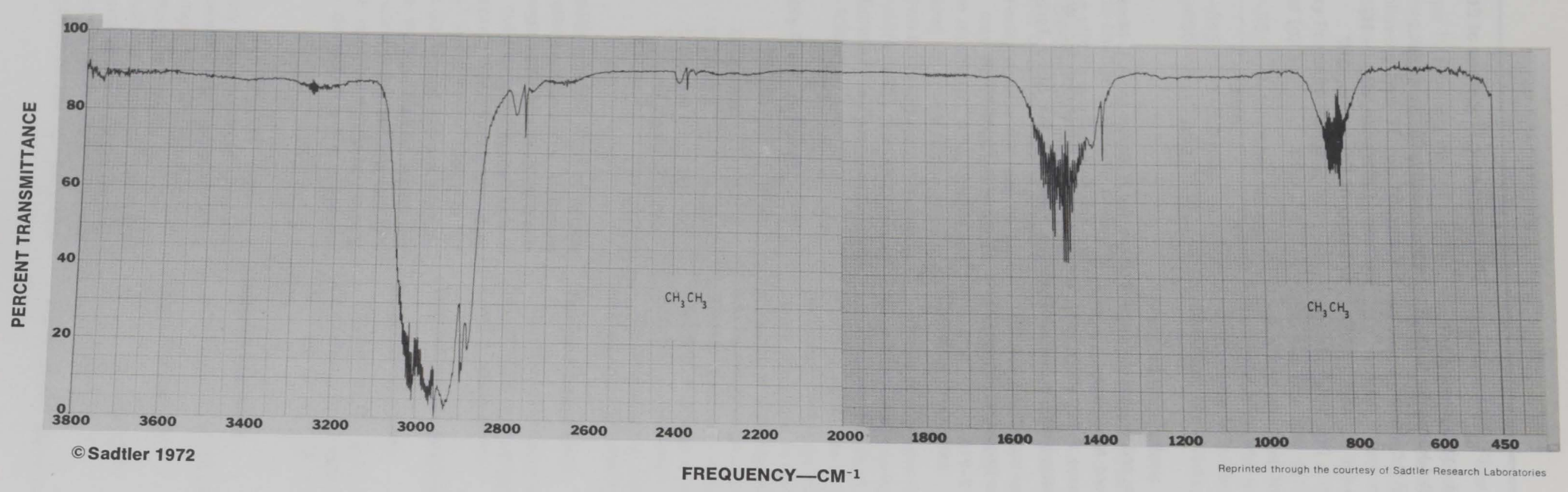
[2] H. E. Tester, *Thermodynamic Functions of Gases*, F. Din, editor, *1961*, Volume 3, p. 194, Butterworth, Inc., Washington, D. C.

[3] D. D. Wagman, *et al.*, *Selected Values of Chemical Thermodynamic Properties*, *1968*, Natl. Bur. Stand. Tech. Note 270-3, U. S. Government Printing Office, Washington, D. C.

[4] **The Sadtler Standard Spectra**, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[5] See reference 2, pp. 199–201, 202–205, 212–215.

[6] See reference 2, p. 179.



Reprinted through the courtesy of Sadtler Research Laboratories

Fig. 2. Infrared spectrum of gaseous ethane over the frequency range 3 800-450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure: 8.0 kPa (60 mmHg) (4).

Matheson®

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED ETHANE LIQUID AND VAPOR (12)

Temperature		Pressure		Entropy J/(mol·°K)		Enthalpy kJ/kg		Latent Heat of Vaporization kJ/kg	Specific Volume m^3/kg		Density kg/m^3	
°K	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
89.88 (T.P.)	−297.89			77.278	278.278	178.896	779.711	600.815	1 518.5		658.5	
90	−297.67			77.362	277.984	179.172	779.571	600.399	1 525.1		655.7	
100	−279.67	0.007 09	0.000 07	84.558	262.416	201.893	790.050	588.157	1 556.0		642.7	
110	−261.67	0.077 01	0.000 76	91.086	248.572	224.658	800.734	576.076	1 587.0		630.1	
120	−243.67	0.350 6	0.003 46	97.069	238.446	247.493	811.728	564.235	1 618.2		618.0	
130	−225.67	1.289	0.012 72	102.591	230.455	270.438	823.124	552.686	1 649.8		606.1	
140	−207.67	3.835	0.037 85	107.738	224.053	293.548	835.061	541.513	1 681.4		594.7	
150	−189.67	9.687	0.095 6	112.592	218.906	316.855	847.234	530.379	1 713.3	4.265×10^6	583.7	0.234 5
160	−171.67	21.481	0.212 0	117.152	214.723	340.397	859.551	519.154	1 745.6	2.042×10^6	572.9	0.489 7
170	−153.67	42.921	0.423 6	121.462	211.251	364.189	871.681	507.492	1 778.8	1.077×10^6	562.2	0.928 1
180	−135.67	78.811	0.777 8	125.562	208.238	388.247	883.203	494.956	1 813.4	6.142×10^5	551.5	1.628
184.52 (B.P.)	−127.53	101.325	1.000	127.319	207.066	399.267	888.630	489.363	1 829.7	4.90×10^5	546.5	2.041
190	−117.67	134.762	1.330	129.494	205.601	412.584	893.804	481.220	1 850.0	3.80×10^5	540.5	2.632
200	−99.67	217.464	2.146	133.302	203.342	437.226	903.170	465.944	1.889 9	2.45×10^5	529.1	4.082
210	−81.67	334.069	3.297	136.984	201.376	462.244	912.103	449.859	1 934.5	1.61×10^5	516.9	6.211
220	−63.67	492.237	4.858	140.541	199.702	487.791	920.773	432.982	1 984.7	1.11×10^5	503.9	9.091
230	−45.67	700.358	6.912	144.056	198.238	514.019	928.590	414.571	2 041.9	78 417	489.7	12.75
240	−27.67	967.755	9.551	147.528	196.899	541.068	935.130	394.062	2 107.1	56 934	474.6	17.56
250	−9.67	1 302.03	12.85	150.959	195.560	569.090	939.627	370.537	2 182.2	42 168	458.3	23.71
260	8.33	1 713.41	16.91	154.390	194.221	598.409	942.674	344.265	2 271.7	31 600	440.2	31.65
270	26.33	2 208.88	21.80	157.904	192.841	629.396	942.631	313.235	2 381.4	23 788	419.9	42.04
280	44.33	2 801.64	27.65	161.544	191.376	662.679	940.544	277.865	2 522.4	17 865	396.4	55.98
290	62.33	3 510.91	34.65	165.435	189.242	699.841	929.511	229.670	2 743.3	12 966	364.5	77.12
300	80.33	4 366.09	43.09	171.167	184.849	755.055	891.747	136.692	3 162.3	8 390	316.2	119.2
305.5 (C.P.)	90.23	4 914.26	48.5	178.490		835.340		0.000	4 713.0		212.18	

Table 2. THERMODYNAMIC PROPERTIES OF ETHANE AS REAL GAS (5)

ENTHALPY, **H**, KJ/MOL; ENTROPY, **S**, J/(MOL·°K); SPECIFIC VOLUME, **V**, DM^3/KG

Pressure kPa	Pressure atm		Temperature, °K 200	220	240	260	280	300	320	340	360	380	400	420	440	460	480	500
101.325	1	H	27.391	28.269	29.221	3.141	31.139	32.182	33.273	34.413	35.602	36.841	38.130	39.469	40.859	42.299	43.788	45.326
		S	210.375	214.559	218.543	222.363	226.062	229.664	233.187	236.643	240.036	243.383	246.688	249.961	253.191	256.387	259.558	262.696
		V	531.8	588.5	644.9	701.0	756.8	812.4	867.8	923.1	978.3	1 033	1 088	1 143	1 198	1 253	1 308	1 363
202.650	2	H	27.212	28.131	29.078	30.054	31.065	32.118	33.216	34.362	35.557	36.801	38.094	39.436	40.828	42.271	43.762	45.303
		S	203.961	208.343	212.451	216.354	220.104	223.739	227.292	230.769	234.178	237.538	240.852	244.133	247.370	250.575	253.747	256.893
		V	258.0	287.9	317.3	346.2	374.8	403.1	431.2	459.3	487.1	514.9	542.6	570.2	597.8	625.4	653.0	680.5
303.975	3	H		27.990	28.968	29.966	30.990	32.054	33.161	34.313	35.513	36.761	38.059	39.403	40.798	42.243	43.737	45.281
		S		204.531	208.781	212.778	216.581	220.255	223.831	227.334	230.761	234.128	237.450	240.735	243.982	247.191	250.370	253.517
		V		187.7	207.9	227.8	247.4	266.7	285.7	304.6	323.3	342.0	360.7	379.2	397.7	416.2	434.7	453.1
506.625	5	H			28.739	29.783	30.838	31.923	33.049	34.216	35.426	36.683	37.987	39.340	40.740	42.189	43.688	45.237
		S			203.887	208.033	211.936	215.690	219.329	222.873	226.333	229.726	233.074	236.375	239.631	242.851	246.040	249.195
		V			120.2	133.1	145.4	157.4	169.2	180.9	192.4	203.8	215.1	226.4	237.6	248.8	260.0	271.1
1 013.250	10	H				29.278	30.432	31.589	32.765	33.969	35.207	36.489	37.815	39.186	40.601	42.062	43.570	45.125
		S				200.887	205.167	209.160	212.948	216.601	220.150	223.614	227.011	230.350	233.639	236.889	240.099	243.270
		V				61.71	68.65	75.18	81.84	88.03	94.10	100.1	106.0	111.8	117.6	123.3	129.0	134.7
2 533.125	25	H					28.852	39.401	31.805	33.166	34.522	35.889	37.288	38.713	40.177	41.681	43.222	44.800
		S					193.263	198.614	203.146	207.271	211.163	214.869	218.438	221.910	225.317	228.656	231.940	235.170
		V					21.28	25.52	28.98	32.10	35.02	37.80	40.46	43.03	45.55	48.03	50.47	52.88
5 066.250	50	H							29.373	31.457	33.168	34.766	36.324	37.874	39.433	41.014	42.621	44.250
		S							191.339	197.669	202.568	206.890	210.886	214.664	218.296	221.811	225.229	228.576
		V							10.12	12.94	15.09	16.90	18.55	20.10	21.57	22.98	24.34	25.67
10 132.500	100	H							24.106	26.860	296.947	32.086	34.162	36.063	37.876	39.653	41.420	43.181
		S							172.703	181.042	189.150	195.635	200.953	205.589	209.811	213.761	217.509	221.116
		V							3.08	3.92	5.27	6.60	7.78	8.82	9.75	10.63	11.44	12.22
15 198.750	150	H							23.630	25.671	27.876	30.157	32.370	34.472	36.471	38.408	40.310	42.191
		S							169.853	176.037	182.372	188.523	194.158	199.263	203.944	208.276	212.321	216.158
		V							2.73	3.06	3.53	4.14	4.81	5.50	6.16	6.78	7.38	7.95
20 265.000	200	H							23.492	25.330	27.268	29.298	31.369	33.434	35.465	37.459	39.430	41.382
		S							168.171	173.741	179.280	184.765	190.088	195.116	199.836	204.275	208.467	212.455
		V							2.55	2.76	3.03	3.37	3.77	4.20	4.65	5.10	5.55	5.97
25 331.250	250	H							23.473	25.210	27.020	28.904	30.852	32.834	34.823	36.813	38.798	40.775
		S							166.925	172.189	177.359	182.452	187.448	192.292	196.916	201.334	205.555	209.594
		V							2.45	2.61	2.81	3.04	3.31	3.61	3.96	4.26	4.59	4.93
30 397.500	300	H							23.518	25.193	26.924	28.723	30.586	32.497	34.437	36.391	38.357	40.344
		S							165.912	171.001	175.945	180.799	185.577	190.238	194.749	199.096	203.292	207.334
		V							2.38	2.52	2.67	2.85	3.05	3.27	3.51	3.76	4.03	4.29
35 463.750	350	H							23.599	25.234	26.913	28.648	30.450	32.310	34.207	36.131	38.076	40.046
		S							165.051	170.004	174.820	179.523	184.138	188.665	193.067	197.338	201.489	205.501
		V							2.33	2.44	2.57	2.71	2.87	3.05	3.24	3.44	3.65	3.87
40 530.000	400	H							23.707	25.314	26.958	27.141	30.400	32.221	34.086	35.979	37.900	39.853
		S							164.285	169.155	173.858	178.456	182.971	187.398	191.711	195.908	199.999	203.986
		V							2.28	2.38	2.49	2.61	2.75	2.89	3.05	3.22	3.39	3.57
45 596.250	450	H							23.831	25.417	27.036	28.698	30.420	32.208	34.041	35.907	37.805	39.738
		S							163.594	168.402	173.033	177.560	181.991	186.334	190.577	194.715	198.753	202.702
		V							2.24	2.33	2.43	2.54	2.66	2.78	2.91	3.05	3.19	3.35
50 662.500	500	H							23.968	25.538	27.136	28.779	30.485	32.248	34.053	35.893	37.769	39.684
		S							162.967	167.737	172.339	176.840	181.188	185.456	189.623	193.702	197.719	201.602
		V							2.21	2.29	2.38	2.48	2.58	2.69	2.80	2.92	3.04	3.17

Matheson®

Table 3. COMPRESSIBILITY FACTORS OF ETHANE (6)

Pressure kPa	Pressure atm	Temperature, °K 350	400	450	500
101.325	1	0.995 4	0.997 1	0.998 1	0.998 7
1 013.250	10	0.953 6	0.970 8	0.980 9	0.987 2
2 026.500	20	0.904 6	0.941 3	0.962 1	0.974 9
4 053.000	40	0.796 1	0.880 8	0.925 6	0.951 5
6 079.500	60	0.670 8	0.819 6	0.890 2	0.930 1
8 106.000	80	0.543 2	0.761 2	0.857 5	0.911 3
10 132.500	100	0.477 7	0.712 2	0.830 0	0.895 7
15 198.750	150	0.513 8	0.661 4	0.790 8	0.873 9
20 265.000	200	0.604 9	0.690 8	0.794 7	0.876 3
25 331.250	250	0.708 4	0.757 8	0.833 2	0.902 5
30 397.500	300	0.813 0	0.837 3	0.888 0	0.943 3
35 463.750	350	0.917 2	0.921 6	0.951 7	0.992 1
40 530.000	400	1.020 1	1.007 8	1.020 0	1.046 6
45 596.250	450	1.122 1	1.094 3	1.090 7	1.104 2
50 662.500	500	1.222 5	1.180 7	1.163 1	1.163 6

Matheson®

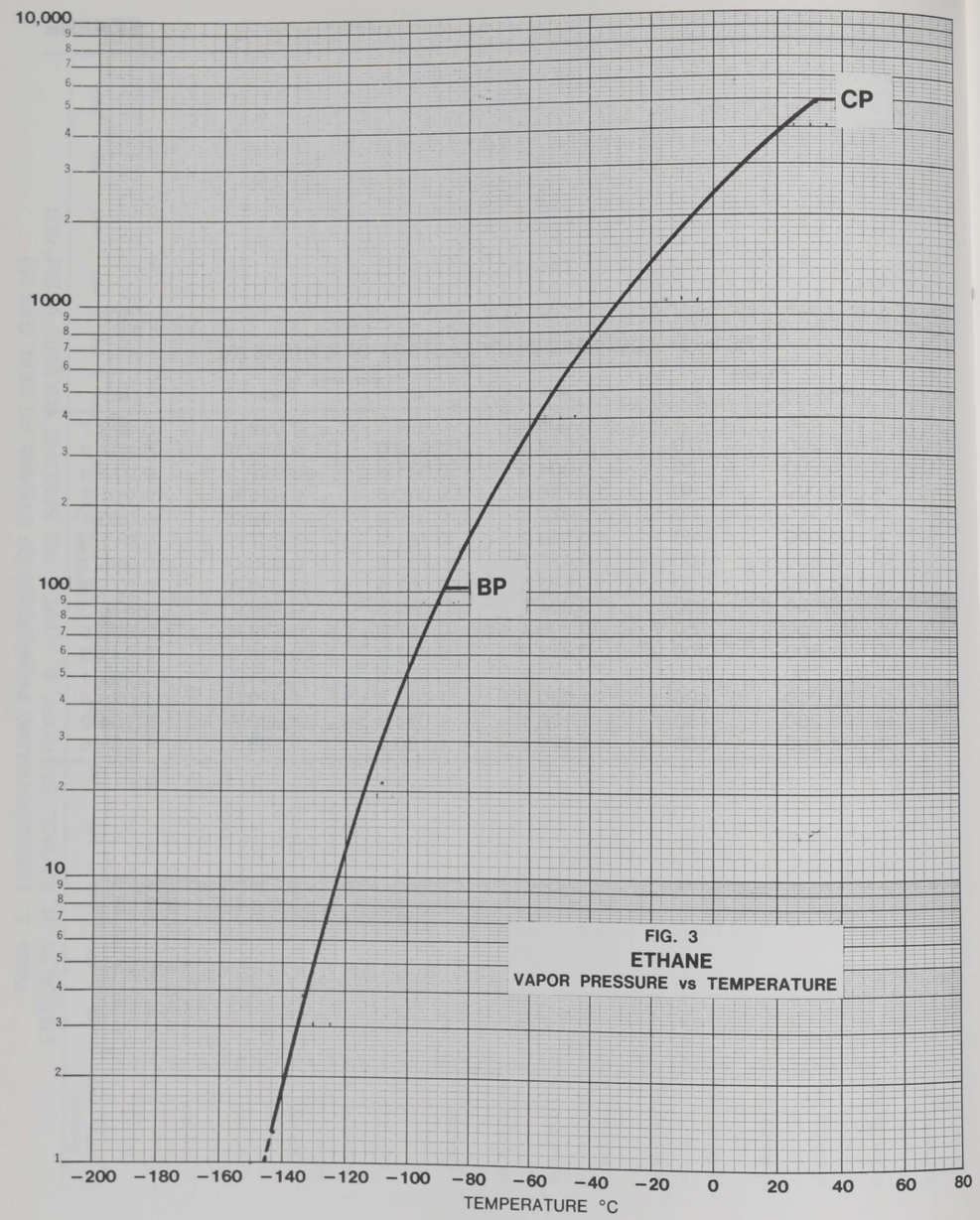


FIG. 3
ETHANE
VAPOR PRESSURE vs TEMPERATURE

Matheson

ETHYLACETYLENE

(Synonym: 1-Butyne)
(Formula: $CH_3CH_2C{:}CH$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.054 092 kg
One Mole of $CH_3CH_2C{:}CH$	0.054 092 kg
Specific Volume @ 21.1 °C, 101.325 kPa	449.5 dm^3/kg; 7.2 ft^3/lb
Vapor Pressure @ 21.1 °C	159.9 kPa; 1.6 bar; 23.2 psia; 1.58 atm
Boiling Point @ 101.325 kPa	281.22 °K; 8.1 °C; 45.5 °F
Triple Point	147.44 °K; −125.7 °C; −194.3 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	2.282 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.93
Density, Liquid @ Saturation Pressure @ 8.1 °C	0.670 kg/l
Critical Temperature	463.70 °K; 190.6 °C; 375.0 °F
Critical Pressure	4 863.6 kPa; 48.64 bar; 705.4 psia; 48.0 atm
Critical Volume	4.001 dm^3/kg
Critical Density	0.249 9 kg/dm^3
Critical Compressibility Factor	0.273
Latent Heat of Fusion @ −125.7 °C	6 029.3 J/mol; 111.5 kJ/kg; 1 441.0 cal/mol
Molar Specific Heat, Gas @ 101.325 kPa @ 15.6 °C	
@ Constant Pressure	79.5 kJ/(kmol·°K); 79.5 J/(mol·°K); 19.00 cal/(mol·°C)
@ Constant Volume	71.2 kJ/(kmol·°K); 71.2 J/(mol·K); 17.02 cal/(mol·°C)
Specific Heat Ratio, Gas @ 101.325 kPa @ 15.6 °C, Cp/Cv	1.117
Molar Specific Heat, Liquid @ 6.8 °C	132.42 kJ/(kmol·°K); 132.42 J/(mol·°K); 31.65 cal/mol·°C)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.007 27 mPa·s; 0.007 27 $mN·s/m^2$; 0.007 27 cP
Viscosity, Liquid @ 0 °C	0.248 mPa·s; 0.248 $mN·s/m^2$; 0.248 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.013 6 W/(m·°K); 32.5 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ 0 °C	0.133 9 W/(m·°K); 32.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 0 °C	20.5 mN/m; 20.5 dyn/cm
Heat of Combustion, Gas @ 25 °C and Constant Pressure	
Gross, to form H_2O (liq) + CO_2 (gas)	2 596.76 kJ/mol
Net, to form H_2O (gas) + CO_2 (gas)	2 464.71 kJ/mol

Description

Ethylacetylene is a colorless, flammable, relatively nontoxic gas at room temperature and atmospheric pressure, with an odor resembling that of acetylene. It is shipped as a liquefied gas under its own vapor pressure of 59 kPa (8.5 psig) at 21.1 °C.

Specifications

Ethylacetylene has a minimum purity of 95.0%.

Uses

Ethylacetylene is used chiefly in organic synthesis.

Matheson

Toxicity

The toxicity of ethylacetylene has not been thoroughly investigated. It probably has some anesthetic activity and can act as a simple asphyxiant by displacing the necessary amount of oxygen to support life.

Precautions in Handling and Storage

The hazards in handling ethylacetylene are mainly due to its flammability. Store and use cylinders of ethylacetylene in well-ventilated areas away from heat and all sources of ignition such as flames and sparks. Never use flames to detect flammable gas leaks, use soapy water. Do not store reserve stocks of cylinders of ethylacetylene with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all lines and equipment used with ethylacetylene.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks in lines and equipment containing ethylacetylene may be detected by applying a soap water solution to the suspected points; leaks will be indicated by a bubble formation.

Disposal of Leaking Cylinders

Cylinders containing ethylacetylene which develop leaks that cannot be corrected normally may be disposed of by the procedure described in Appendix II-A.

Materials of Construction

Steel and stainless steel are satisfactory for handling ethylacetylene. Copper or metals capable of forming explosive acetylides should not be used with ethylacetylene either in process lines or in control equipment.

Cylinder and Valve Description

Ethylacetylene is packed in DOT approved, low pressure steel cylinders. Cylinders of ethylacetylene are equipped with valves having Compressed Gas Association (CGA) valve outlet connection No. 510, the approved standard, which has a thread size of 0.885 inch diameter, with left-hand internal threads accepting a bullet-shaped nipple (see Figure 1). Lecture bottles have a special $^{5}/_{16}$ inch-32 threads per inch female outlet and a $^{9}/_{16}$ inch-18 threads per inch male dual valve outlet.

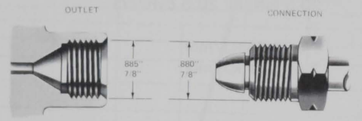


Fig. 1. CONNECTION 510 .885"-14 LH INT. accepting a Bullet Shaped Nipple

Safety Devices

Cylinders of ethylacetylene have, as safety devices, spring-loaded safety relief valves. This type of device will release gas if the cylinder pressure becomes excessive, and will close when the pressure is restored to a safe value.

Recommended Controls

Manual Controls

Matheson needle valve Model 61-510, of stainless steel, is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, ¼" compression fitting, or ¼" NPT male or female pipe. A Model 32 manual needle valve can be supplied for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one form the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Ethylacetylene is classified by the DOT as a flammable liquid, and is shipped with the required "Red Label".

Commercial Preparations

Ethylacetylene is prepared by reacting sodium acetylide with diethyl sulfate. It may also be obtained by treating 1,2- or 1,1-dibromobutane with alcoholic potassium hydroxide.

Chemical Properties

Ethylacetylene exhibits the typical properties of acetylenes. For more complete data see the chemical properties of acetylene, contained in the Matheson Unabridged Gas Data Book.

Thermodynamic and Detailed Physical Data

Molecular Structure

The atomic parameters for this linear molecule are as follows (2): —C—C≡1.462 Å (1.462×10^{-10} m); —C≡C— 1.207 Å (1.207×10^{-10} m); ≡C—H 1.06 Å (1.06×10^{-10} m); —C—C— 1.54 Å (1.54×10^{-10} m); methylene C—H 1.1 Å (1.1×10^{-10} m); methyl C—H 1.09 Å (1.09×10^{-10} m).

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous ethylacetylene.

Vapor Pressure

Vapor pressure values between 194.40 and 282.71°K are listed below (2).

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
194.40	0.523	5.2	3.92
204.25	1.232	12.3	9.24
214.44	2.738	27.4	20.54
224.48	5.552	55.5	41.64
236.75	11.952	119.5	89.65
249.30	23.974	239.7	179.8
258.72	38.314	383.2	287.4
267.32	56.847	568.5	426.4
275.88	81.807	818.1	613.6
281.22	101.304	1 013.0	759.8
282.71	107.346	1 073.5	805.2

Vapor pressure values above 101.325 kPa (1 atm) are shown below (3).

Temperature, °K	Vapor Pressure kPa	bar	atm
281.23	101.325	1.013	1.000
283.15	113.788	1.14	1.123
293.15	153.102	1.53	1.511
298.15	179.953	1.80	1.776
313.15	279.252	2.79	2.756
333.15	482.611	4.83	4.763
353.15	813.538	8.14	8.029
373.15	1 241.029	12.4	12.25
393.15	1 702.969	17.0	16.81
413.15	2 507.719	25.1	24.77
433.15	3 378.378	33.8	33.34
453.15	4 309.251	43.1	42.53

See Figure 3 for vapor pressure vs. temperature curve.

Latent Heat of Vaporization, ΔHv (2)

Temperature, °C	ΔHv, kJ/kg
−10.6	476.99
3.8	458.54
8.2	453.56

Thermodynamic Properties of Ethylacetylene As Ideal Gas

Heat Capacity, C_p° (1) @ 25 °C	81.170 J/(mol·°K)
Entropy, S° (2) @ 8.1 °C	291.28 J/(mol·°K)
Enthalpy of Formation, ΔH_f° (4) @ 25 °C	165.18 kJ/mol
Free Energy of Formation, ΔF_f° (4) @ 25 °C	202.09 kJ/mol

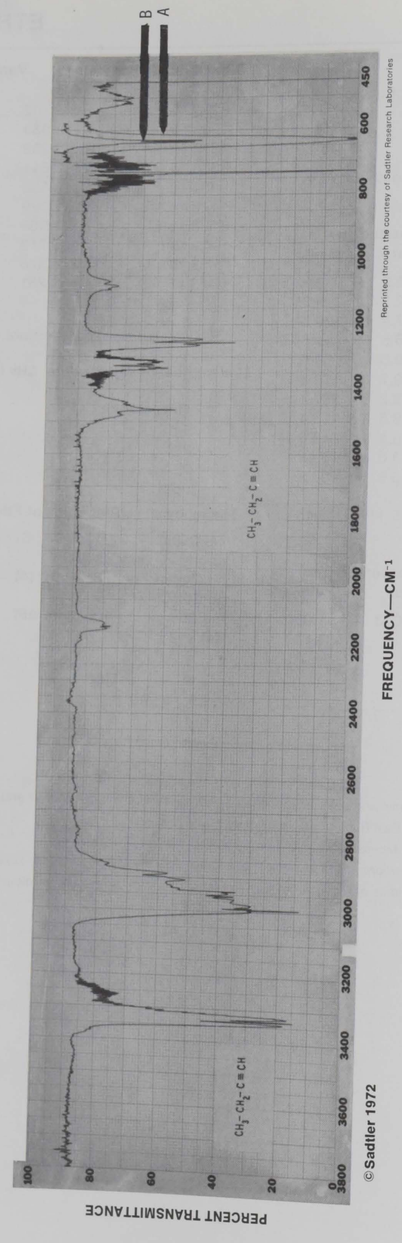
REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of ethylacetylene, see W. Barker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] J. G. Aston, S. V. R. Mastrangelo, and G. W. Moessen, *J. Amer. Soc. 72*, 5287–5291 (1950).

[3] R. W. Gallant, *Physical Properties of Hydrocarbons, 1968*, Volume 1, p. 21, Gulf Publishing Co., Houston, Texas.

[4] C. E. Miller and F. D. Rossini, *Physical Constants of Hydrocarbons*, C_1 to C_{10}, *1961*, p. 29, American Petroleum Institute, New York, New York.



©Sadtler 1972
Reprinted through the courtesy of Sadtler Research Laboratories

Fig. 2. Infrared spectrum of gaseous ethylacetylene over the frequency region 3 800 cm^{-1} to 450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure: curve A (complete scan): 6.666 kPa (50 mmHg), curve B (partial scan): 0.667 kPa (5 mmHg) (15). Note: The 730 cm^{-1} band is an impurity.

Matheson

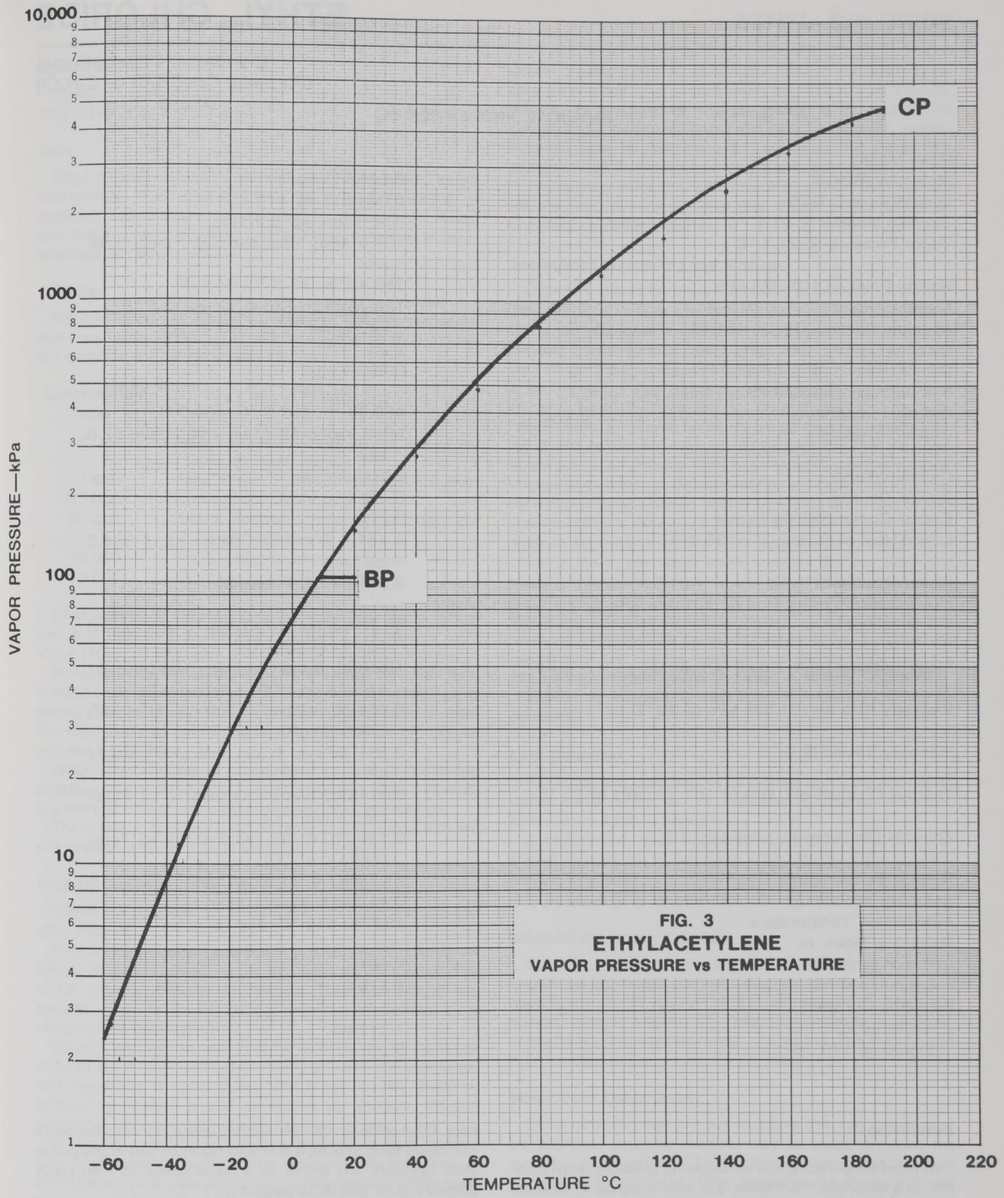


FIG. 3
ETHYLACETYLENE
VAPOR PRESSURE vs TEMPERATURE

Matheson

ETHYL CHLORIDE

(Synonym: Chloroethane)
(Formula: CH_3CH_2Cl or C_2H_5Cl)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.064 515 kg
One Mole of C_2H_5Cl	0.064 515 kg
Specific Volume @ 21.1 °C, 101.325 kPa	374.6 dm^3/kg; 6 ft^3/lb
Vapor Pressure @ 21.1 °C	137.9 kPa; 13.8 bar; 20.0 psia; 1.36 atm
Boiling Point @ 101.325 kPa	285.42 °K; 12.3 °C; 54.1 °F
Freezing Point	136.75 °K; −136.4 °C; −213.5 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	2.642 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	2.23
Density, Liquid @ Saturation Pressure @ 25 °C	0.890 9 kg/l
(For additional liquid density values, see Table 1.)	
Critical Temperature	460.35 °K; 187.2 °C; 369.0 °F
Critical Pressure	5268.9 kPa; 52.7 bar; 764.2 psia; 52.0 atm
Critical Volume	3.100 dm^3/kg
Critical Density	0.3226 kg/dm^3
Critical Compressibility Factor	0.275
Latent Heat of Fusion @ −136.4 °C	4 451.8 J/mol 69.004 kJ/kg; 1 064.0 cal/mol
Flammable Limits In Air	3.8–15.4% (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	65.73 kJ/(kmol·°K); 65.73 J/(mol·°K) 15.71 cal/(mol·C°)
Molar Specific Heat, Liquid @ 6.8 °C	102.090 kJ/(kmol·°K); 102.090 J/(mol·°K); 24.400 cal/(mol·°C)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.009 50 mPa·s; 0.009 50 $mN·s/m^2$; 0.009 50 cP
Viscosity, Liquid @ 0 °C	0.331 mPa·s; 0.331 $mN·s/m^2$; 0.331 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.011 088 W/(m·°K); 26.5×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ 0 °C	0.129 703 W/(m·°K); 310.0×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 0 °C	21.5 mN/m; 21.5 dyn/cm
Solubility in Water @ 101.325 kPa @ 0 °C	0.447 kg C_2H_5Cl/100 kg H_2O
Autoignition Temperature	792 °K; 519 °C; 966 °F
Refractive Index, n_D	
Vapor @ 25 °C	1.001
Liquid @ 0 °C	1.379 8
Dielectric Constant	
Vapor @ 23.5 °C	1.012 85
Liquid @ 170 °C	6.29

Description

At room temperature and atmospheric pressure, ethyl chloride is a colorless, flammable gas with a pungent, ethereal odor. Ethyl chloride has narcotic properties, but over-exposure can cause toxic effects. It is readily liquefied and is shipped in steel cylinders and drums as a liquid under its own vapor pressure of 37 kPa (5.36 psig) at 21.1 °C.

Specifications

Matheson supplies ethyl chloride having a minimum purity of 99.7% (liquid phase).

Uses

Ethyl chloride is used industrially as a refrigerant, as an intermediate in organic synthesis, as a local anesthetic in medicine and dentistry, as a solvent for phosphorus, sulfur, fats, oils, resins, and waxes, and for the manufacture of tetraethyllead and ethylcellulose.

Toxicity

Ethyl chloride has narcotic properties, but over-exposure can cause toxic effects. The effects of ethyl chloride in man are shown in the following table (2).

Concentration ppm	Effects
40 000	After 2 inhalations, stupor, irritation of the eyes, stomach cramps
33 600	After 30 sec. quickly increasing toxic effect
25 000	Lack of coordination
20 000	After 4 inhalations, dizziness and slight abdominal cramps.
19 000	Weak analgesia after 12 minutes
13 000	Slight symptoms of poisoning

Ethyl chloride is the least toxic of all the chlorinated hydrocarbons. The 1979 ACGIH has established a Threshold Limit Value (TLV) of 1 000 ppm (2600 mg/m^3) for ethyl chloride.

Because of its very rapid evaporation, ethyl chloride has a marked cooling effect on the skin. Continued contact with rapid evaporation from the skin can produce frostbite. Aside from this it acts only as a mild and temporary irritant to the skin or mucous membranes.

When ethyl chloride is decomposed by heat, hydrochloric acid may be one of the decomposition products. This, if inhaled, is a marked irritant to the respiratory mucous membranes.

There are no serious health hazards in connection with the use of ethyl chloride if good ventilation is provided.

First Aid Suggestions (3)

Summon a physician for anyone who has been overcome by ethyl chloride.

Prior to the physician's arrival first aid measures should be taken. Those presented herein are based on what is believed to be common practice in industry. Their adoption in any specific case should be subject to prior endorsement by a competent medical advisor.

Usually, recovery is prompt, if the victim is quickly removed to fresh air. If the exposure has been extreme and extended, and the victim is unconscious and breathing has stopped, artificial respiration should be started immediately. Oxygen should be administered by trained personnel only.

In case of severe exposure, and especially if ethyl chloride may have been decomposed by heat with the formation of hydrochloric acid, pulmonary edema may develop. After such exposure, inhalation of 100% oxygen is indicated. The patient should breathe 100% oxygen under positive exhalation pressure for one-half hour periods every hour for at least 3 hours. If there are no signs of lung congestion at the end of this period, and if breathing is easy and the color is good, oxygen inhalation may be discontinued. Throughout this period, the patient should be kept comfortably warm, but not hot.

Any stimulants for shock treatment should be given only by the attending physician. Never give anything by mouth to an unconscious patient.

Precautions in Handling and Storage

Cylinders should be firmly supported to prevent movement. The cylinder should be grounded to discharge any static electricity. All connections should be made tight. Work should be done in a well-ventilated area, preferably a hood with forced ventilation. The cylinder should never be directly connected to a container of liquid, since suckback can occur causing a reaction within the cylinder. To prevent suckback, a trap, check-valve, or vacuum break should be inserted into the line. An air-line or oxygen mask should be kept close by the operations site, in an area not likely to be contaminated, to be used in case of emergency. Because of fire and explosion hazards, cylinders of ethyl chloride should be stored and used only in well-ventilated areas away from heat and all sources of ignition such as flames and sparks. Never use flames to detect ethyl chloride leaks, use soap water solution. Do not use ethyl chloride around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of ethyl chloride cylinders with cylinders containing oxygen, chlorine, other highly oxidizing or flammable materials. Safety showers should be readily available, and fire-fighting hand operated extinguishers of an approved type should be placed in strategic locations.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

All fittings and joints should be painted with soap solution to detect leaks, which will be indicated by bubble formation. Never use a flame to detect leaks.

A commercial, explosion-proof combustible gas indicator should be available to determine ethyl chloride vapor concentrations in manufacturing buildings or around equipment which is to be repaired or to locate sources of small leaks.

Disposal of Leaking Cylinders

Cylinders containing ethyl chloride which develop leaks that cannot be corrected normally may be connected with the appropriate needle valve and the vapor or liquid absorbed in a suitable organic solvent, e.g., methanol, methylene chloride, chloroform, carbon tetrachloride, or benzene. The solution can then be disposed of or used for recovery of the ethyl chloride.

Materials of Construction

Since ethyl chloride is a noncorrosive gas, any common or commercially available material may be used, provided the system is dry; moisture will cause the development of corrosive conditions, especially at higher temperatures. Piping systems or vessels to contain ethyl chloride should be adequately

designed and totally enclosed for processes using ethyl chloride as an intermediate. Appropriate relief devices should be installed to prevent excessive pressure from building up.

Cylinder and Valve Description

Ethyl chloride is shipped in DOT approved, low pressure steel cylinders and drums. Cylinders of ethyl chloride are equipped with brass valves having Compressed Gas Association (CGA) valve outlet No. 510 as standard, or the No. 300 as alternate, with a thread size of 0.885 inch diameter, right-hand external threads, accepting a bullet-shaped nipple. (See Figure 1 for an illustration of this valve outlet and its mating connection). Lecture bottles have a special $^{5}/_{16}$"-32 threads per inch,

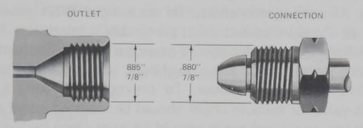


Fig. 1. CONNECTION 510 .885"-14 LH INT. accepting a Bullet Shaped Nipple

female valve outlet and a $^{9}/_{16}$"-18 threads per inch male dual valve outlet.

Safety Devices

No safety devices are used on drums of ethyl chloride. Do not store drums near any sources of heat. Cylinders are equipped with valves having fuse plug safety devices.

Recommended Controls

Manual Controls

Matheson needle valve Model 50-300, a brass bar stock valve, is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, ¼" compression fitting, or ¼" NPT male or female pipe. A Model 31B manual needle valve can be supplied for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass flowmeter units with 65 mm tubes with a single float, are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Ethyl chloride is classified by the DOT as a flammable liquid and is shipped with the required "Red Label".

Commercial Preparations

Ethyl chloride is obtained as a by-product in the manufacture of chloral. It is also obtained by passing hydrogen chloride into a mixture of ethyl alcohol and zinc chloride and by treating ethylene with hydrogen chloride at −80 °C in the presence of aluminum chloride and ethyl chloride as a solvent. It may also be prepared by treating ethyl alcohol with phosphorus trichloride or thionyl chloride. It is also prepared by vapor phase hydrochlorination of ethylene at 125–250 °C under a variety of catalytic conditions.

Chemical Properties

In the series of normal saturated alkyl chlorides, bromides, and iodides, the methyl compound is the most reactive and the reactivity remains essentially constant from the ethyl homolog on. Also, in the same series, the iodide is more reactive than the corresponding bromide which in turn is more reactive than the chloride. In general, the alkyl halides react with magnesium (Grignard), reducing agents, sodium (Wurtz), sodium alkoxides (Williamson), alcoholic potassium hydroxide (formation of alkenes), and silver hydroxide (alcohol formation). They also react with the sodium derivatives of malonic and acetoacetic esters, with potassium hydrosulfide, ammonia, lithium, zinc, metal cyanides, and with salts of carboxylic acids. However, n- and sec-alkyl halides are hydrolyzed less readily than tert-alkyl halides.

Thermodynamic and Detailed Physical Data

Molecular Structure

Ethyl chloride is a polar, nonlinear molecule of D_{3d} symmetry, having the following interatomic distances: C—C: 1.54 Å (1.54 × 10^{-10} m); C—H: 1.09 Å (1.09 × 10^{-10} m); C—Cl: 1.75 Å (1.75 × 10^{-10} m) (1).

Infrared Spectrum

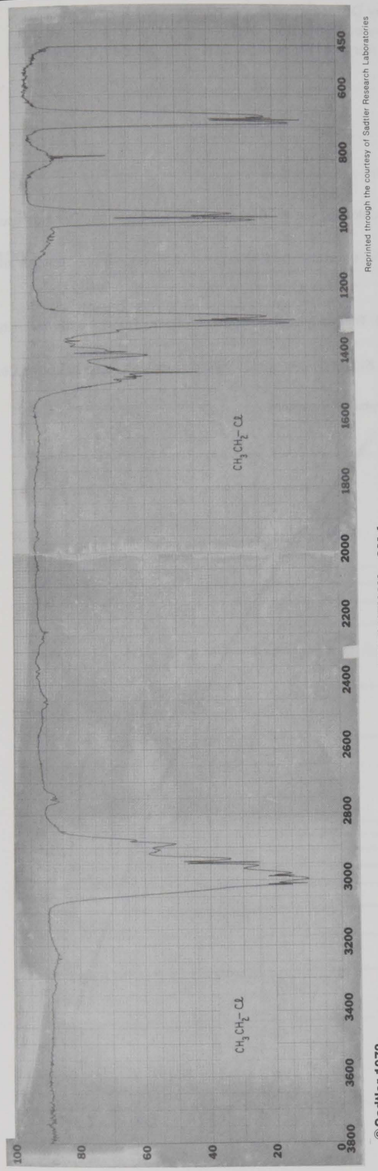
See Figure 2 for the infrared spectrum of gaseous ethyl chloride.

Vapor Pressure

Vapor pressure values up to 101.325 kPa (1 atm) (760 mmHg) have been calculated by the following Antoine vapor pressure equation (4):

$$\log_{10} p = A - \frac{B}{C + t} \quad \text{or} \quad t = \frac{B}{A - \log_{10} p} - C$$

Matheson



Reprinted through the courtesy of Sadtler Research Laboratories
©Sadtler 1972

Fig. 2. Infrared spectrum of gaseous ethyl chloride in the frequency range 3 800–450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure (complete scan): 6 666 kPa (50 mmHg) (6).

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.949 14, 1 012.771, and 236.67, respectively.

The following vapor pressures have been calculated by the above equation.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
206.72	1.333	13.3	10
215.79	2.666	26.7	20
221.56	4.000	40.0	30
225.89	5.333	53.3	40
229.38	6.666	66.7	50
232.34	7.999	80.0	60
237.19	10.666	106.7	80
241.12	13.332	133.3	100
248.67	19.998	200.0	150
254.37	26.664	266.6	200
259.01	33.331	333.3	250
262.95	39.996	400.0	300
269.46	53.328	533.3	400
274.77	66.661	666.6	500
279.29	79.993	800.0	600
283.25	93.326	933.3	700
285.42	101.325	1 013.25	760

Vapor pressure values above 101.325 kPa (1 atm) are listed below (5).

Temperature, °K	Vapor Pressure kPa	bar	mmHg
286.79	106.658	1.07	800
292.93	133.321	1.33	1 000
304.90	199.983	2.00	1 500
337.15	506.625	5.07	3 800
365.75	1 013.250	10.1	7 600
400.45	2 026.500	20.3	15 200
422.65	3 039.750	30.4	22 800
440.15	4 053.000	40.5	30 400
453.65	5 066.250	50.7	38 000
460.35 (C.T.)	5 268.900	52.7	39 520(C.P.)

For additional vapor pressure data, see Figure 3.

Latent Heat of Vaporization, ΔHv (1)

Temperature, °C	ΔHv, kJ/kg
0	392.05
12.3	382.11
20	375.66

Matheson

ETHYL CHLORIDE

Thermodynamic Properties of Ethyl Chloride As Ideal Gas @ 25 °C (4)			
Heat Capacity, C_p°	62.760 J/(mol·°K)	Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	13.292 kJ/mol
Entropy, S°	275.934 J/(mol·°K)	Enthalpy of Formation, ΔH_f°	−107.529 kJ/mol
		Gibbs Energy of Formation, ΔG_f°	−55.647 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of ethyl chloride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, East Rutherford, New Jersey.

[2] K. B. Lehmann and F. Flury, *Toxicology and Hygiene of Industrial Solvents, 1934*, translated by E. King and H. F. Smyth, Jr., Williams and Wilkins, Baltimore, Maryland.

[3] *Data Sheet SD-50*, Manufacturing Chemists' Association, Inc., Washington, D. C.

[4] B. J. Zwolinski, **et al.**, *Selected Values of Properties of Chemical Compounds, 1968*, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[5] *Chemical Engineers' Handbook*, 4th edition, R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, editors, *1963*, p. 3-60, McGraw-Hill Book Co., Inc., New York, New York.

[6] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[7] See reference 5, p. 3-164.

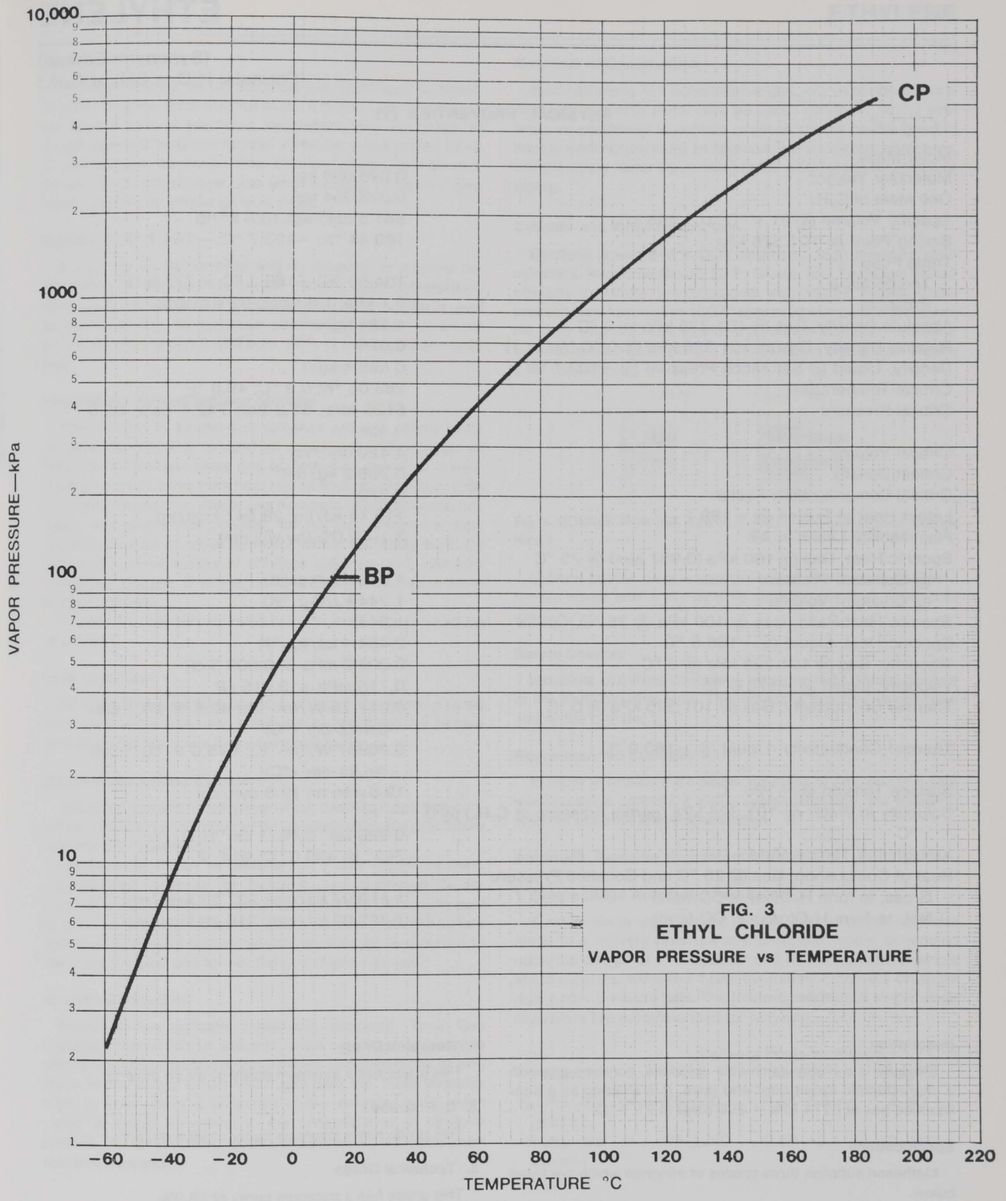


FIG. 3
ETHYL CHLORIDE
VAPOR PRESSURE vs TEMPERATURE

ETHYLENE

(Synonym: Ethene)
(Formula: $H_2C = CH_2$ or C_2H_4)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.028 054 kg
One Mole of C_2H_4	0.028 054 kg
Specific Volume @ 21.1 °C, 101.325 kPa	861.5 dm^3/kg; 13.8 ft^3/lb
Boiling Point @ 101.325 kPa	169.44 °K; −103.7 °C; −154.7 °F
Triple Point	
Temperature	104.00 °K; −169.2 °C; −272.5 °F
Pressure	0.1 kPa; 1.0 mbar; 0.76 mmHg
Absolute Density, Gas @ 101.325 kPa @ 0 °C	1.261 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 0 °C (Air = 1)	0.975
Density, Liquid @ Saturation Pressure @ −103.7 °C	0.568 4 kg/l
Critical Temperature	283.05 °K; 9.9 °C; 49.8 °F
Critical Pressure	5120 kPa; 51.2 bar; 742.1 psia; 50.5 atm
Critical Volume	4.420 dm^3/kg
Critical Density	0.266 2 kg/dm^3
Critical Compressibility Factor	0.270
Latent Heat of Fusion @ −169.2	119.44 kJ/kg; 28.547 kcal/kg
Flammability Limits in Air	3.1–32.0% (by volume)
Specific Heat, Gas @ 100 kPa (0.987 atm) @ 25 °C	
@ Constant Pressure	1.548 kJ/(kg·°K)
@ Constant Volume	1.244 kJ/(kg·°K)
Specific Heat Ratio, Gas @ 100 kPa @ 25 °C, Cp/Cv	1.244
Specific Heat, Liquid @ −166.5 °C	2.464 4 kJ/kg·°K
Viscosity, Gas @ 101.325 kPa @ 0 °C	0.009 2 mPa·s; 0.009 3 cP
Viscosity, Liquid @ −170.0 °C	0.715 mPa·s; 0.715 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 0 °C	0.017 78 W/(m·°K); 42.5 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −160.0 °C	0.26987 W/(m·°K); 645.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −120 °C	19.8 mN/m; 19.8 dyn/cm
Solubility in Water @ 101.325 kPa (partial pressure of C_2H_4) @ 0 °C	0.226 cm^3 C_2H_4/1 cm^3 H_2O
Autoignition Temperature	763° K; 490.0 °C; 914 °F
Heat of Combustion, Gas @ 25 °C and Constant Pressure	
Gross, to form H_2O(liq) + CO_2(gas)	1 410.97 kJ/mol; 337.23 kcal/mol
Net, to form H_2O(gas) + CO_2(gas)	1 322.98 kJ/mol; 316.20 kcal/mol

Description

Ethylene is a highly flammable colorless, nontoxic gas with a characteristic sweet odor and taste. It is shipped as a non-liquefied gas at 8274 kPa (1 200 psig) at 21.1 °C.

Specifications

Matheson supplies three grades of ethylene which are listed below.

1. **Research Grade**

This grade has a minimum purity of 99.98 mole %.

2. **C. P. Grade**

This grade has a minimum purity of 99.5 mole %.

3. **Technical Grade**

This grade has a minimum purity of 98.0%.

Uses

Ethylene is used for accelerating the ripening of bananas, and maturing the color of citrus fruits. It is also used to increase the growth rate of seedlings, vegetables, and fruit trees; in oxyethylene welding and cutting of metals; in the manufacture of mustard gas, ethylene oxide, ethylene glycol, ethyl alcohol, polyethylene, polystyrene, and other plastics; in organic synthesis; and as an inhalation anesthetic.

Toxicity (2)

Except for its flammability and its property of causing asphyxiation by lowering the oxygen content of the atmosphere, ethylene is not hazardous. Ethylene mixed with oxygen is used as an anesthetic. Its maximum permissible limit in workroom air should not exceed 5 500 ppm, 20% of the lower flammable limit.

Precautions in Handling and Storage

The hazards in handling of ethylene are due chiefly to its extreme flammability. Ground all equipment and cylinders of ethylene before use. Store and use ethylene cylinders in well-ventilated areas away from heat and all sources of ignition such as flames and sparks. Never use flames to detect ethylene gas leaks, use soap water solution. Do not use ethylene around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of ethylene cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

All fittings and joints suspected of leaks should be painted with soap water solution; leaks will be indicated by bubble formation. Do not use a flame to detect leaks.

Disposal of Leaking Cylinders

Cylinders containing ethylene which develop leaks that cannot be corrected normally may be disposed of by the procedure described in Appendix II-A.

Alternatively, it can be dissolved in a cold organic solvent, e.g., alcohol, acetone, or benzene, and subsequently recovered by warming or it can be absorbed in 95% sulfuric acid by which it is mainly converted into a mixture of diethyl sulfate and ethyl hydrogen sulfate, which can then be transferred to the plant disposal unit for neutralization and disposal.

Analytical Detection

Matheson has available a manually operated "Toxic Gas Detector" Model 8014K which provides accurate, dependable and reproducible results in determining concentrations of ethylene in the range of 0.1–100 ppm with the 108B detector tube. A color stain is produced in the detector tube which varies in length according to the concentration of ethylene present, the length being measured against a calibration chart which is supplied.

Materials of Construction

Since ethylene is a noncorrosive gas, any common or commercially available metal may be used. However, piping systems, or equipment to contain ethylene should be designed to have a working pressure as specified by competent engineers, using a safety factor conforming to the ASME code for pressure piping.

Cylinder and Valve Description

Ethylene is supplied in DOT approved, high pressure steel cylinders. Research Grade, C. P. Grade, and Technical Grade ethylene cylinders are equipped with valves having Compressed Gas Association (CGA) approved standard valve outlet No. 350 with a thread size of 0.825 inch diameter, left-hand external threads accepting a round shaped nipple (see Figure 1 for illustration).

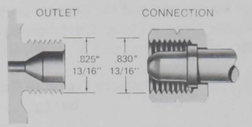


Fig. 1. CONNECTION 350 .825"-14 LH EXT. accepting Round Shaped Nipple

Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet and a 9/16 inch-18 threads per inch male dual valve outlet.

Safety Devices

Industrial cylinders containing ethylene have safety devices of the frangible disc type. This device is required in only one end of the cylinder.

Recommended Controls

In order to reduce the cylinder pressure of ethylene to a safe working value consistent with a system's design, the following types of controls are recommended.

Automatic Pressure Regulators

1. Single Stage Automatic Regulators

A single stage regulator will reduce cylinder pressure in one stage to a delivery pressure in a particular range, depending upon the design of the regulator and its spring load. A single stage regulator will show a slight variation in delivery pressure as cylinder pressure falls. The following Matheson single stage regulators are recommended for ethylene:

Model No.	Delivery Pressure Range kPa	bar (g)	psig
1L-350 (for all grades)	28–550	0.28–5.5	4–80
1H-350 (for all grades)	69–1240	0.69–12.4	10–180

Model No.	Delivery Pressure Range kPa	bar (g)	psig
2-350 (for C.P. and Technical Grades)	340–4 480	3.4–44.8	50–650
3-350 (for C.P. and Technical Grades)	690–10 340	6.9–103.4	100–1 500
3320 (for lecture bottles containing C. P. and Technical Grades)	28–410	0.28–4.1	4–60

2. Two Stage Automatic Regulators

This type of regulator performs the same function as a single stage regulator. However, greater accuracy in control of delivery pressure is maintained and the delivery pressure does not vary when cylinder pressure falls. The following Matheson two stage regulators are recommended for ethylene:

Model No.	Delivery Pressure Range kPa	bar (g)	psig
8L-350	14–104	0.14–1.04	2–15
8-350	28–340	0.28–3.4	4–50
8H-350	69–690	0.69–6.9	10–100
9-350	138–1720	1.38–17.2	20–250

3. Low Pressure Regulator

Accurate delivery pressures, ranging from 2 inches water column to 10 psig, can be obtained from Matheson Model 70 low pressure regulators. This regulator has an oversize, pancake body of die cast aluminum and a Buna N diaphragm. The following models are available.

Model No.	Delivery Pressure Range kPa	mbar (g)	psig
70B	0.5–3.0	5–30	2–12 inches water column
70	3.5–34.5	34–345	0.5–5.0 psig
70A	34.5–68.9	345–689	5–10 psig

Model 70 regulators are rated for a maximum inlet pressure of 1 720 kPa (250 psig). Excellent results are obtained by reducing the high cylinder pressure of ethylene to 170–550 kPa (25–80 psig) with a pressure regulator, such as Matheson Model 1L-350, and delivering this pressure to the Model 70 regulator. When so used, the two regulators can be connected with a heavy duty hose and the proper fittings, which are available as a unit.

Manual Controls (for all grades)

Manual needle valves Models 50-350 and 52-350 with tank gauge are available for direct attachment to the cylinder valve outlet. These valves can be equipped with a variety of outlets, such as a serrated hose end, ¼" compression fitting, or ¼" NPT male or female pipe. These types of controls are used chiefly when intermittent flows are necessary, or to control the flow of gas directly from the cylinders but they require close supervision. They should not be used as pressure controls since dangerous pressures can develop if a line or system becomes clogged.

Models 30AR and 31B are recommended for use with lecture bottles containing C.P. and Technical Grades.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure or temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Ethylene is shipped in high pressure steel cylinders as a flammable, compressed gas taking a DOT "Red Gas Label".

Chemical Preparations

(a) Ethylene is obtained in the cracking of petroleum gas.

(b) Ethylene is produced by passing ethyl alcohol vapors over dehydrating catalysts at 360–470 °C.

(c) In the laboratory, ethylene may be conveniently prepared by the action of sulfuric or phosphoric acid on ethyl alcohol at 170–220 °C.

(d) Ethylene may be obtained by the pyrolysis of ethane above 500 °C with or without a catalyst.

(e) Small quantities of ethylene may be prepared by treating an alcoholic solution of ethylene bromide with zinc or zinc-copper couple.

Chemical Properties

Ethylene undergoes the following reactions:

(a) Under high temperatures and pressures, it is polymerized to polyethylene.

(b) On catalytic hydrogenation, it forms ethane.

(c) It combines with halogen acids forming alkyl halides.

(d) It combines with sulfuric acid forming ethyl hydrogen sulfate, which, on hydrolysis, yields alcohol.

(e) It combines with chlorine, bromine, and iodine as well as iodine monochloride forming dihalides.

(f) It reacts with hypohalous acid yielding halohydrins.

(g) Careful oxidation with dilute potassium permanganate yields ethylene glycol.

(h) On catalytic oxidation, it yields ethylene oxide.

(i) With ozone, it forms an ozonide.

(j) With sulfur monochloride, it forms mustard gas, di-(2-chloroethyl) sulfide.

(k) It reacts with acyl halides in the presence of aluminum chloride to give 2-chloroethyl ketones.

(l) Ethylene is used in the Prins reaction with formaldehyde in acetic acid to produce 1,3-propanediol diacetate, which can be hydrolyzed to 1,3-propanediol which was previously available mainly by fermentation of glycerol.

Thermodynamic and Detailed Physical Data

Molecular Structure

The ethylene molecule is planar, with D_{2h} symmetry and a symmetry number of four. The C=C bond distance is 1.337 Å (1.337×10^{10} m), the C—H bond distance 1.086 Å (1.086×10^{-10} m). The H—C—H bond angle is 117.37°, the H—C=C bond angle is 121.32° (1).

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous ethylene.

Vapor Pressure

Vapor pressure up to 101.325 kPa (1 atm) is listed below (3).

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
104.85	0.133	1.33	1
114.85	0.667	6.67	5
119.95	1.333	13.3	10
125.55	2.666	26.7	20
131.85	5.332	53.3	40
135.85	7.998	80.0	60
141.35	13.330	133.3	100
149.75	26.660	266.6	200
159.25	53.320	533.3	400
169.45 (B.P.)	101.325	1 013.25	760

Vapor pressure above 101.325 kPa (1 atm) is shown below (4).

Temperature, °K	Vapor Pressure kPa	bar	atm
169.45(B.P.)	101.325	1.013 25	1
182.35	202.650	2.03	2
202.05	506.625	5.07	5
220.35	1 013.250	10.1	10
244.05	2 026.500	20.3	20
258.95	3 039.750	30.4	30
271.65	4 053.000	40.5	40
282.05	5 066.250	50.7	50
283.05 (C.T.)	5 116.913(C.P.)	51.2	50.5

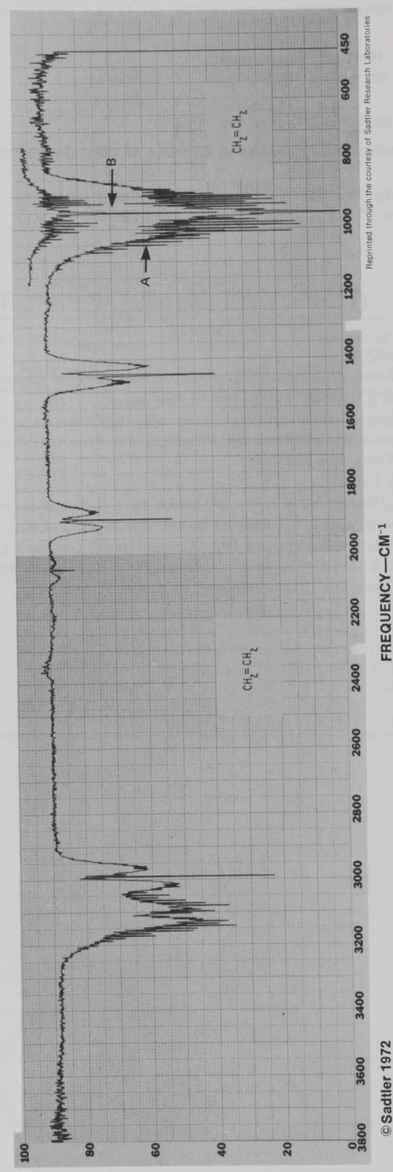


Fig. 2. Infrared spectrum of gaseous ethylene over the frequency of 3 800 cm^{-1} to 450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure: curve A (complete scan): 9.33 kPa (70 mmHg, curve B (partial scan): 1.33 kPa (10 mmHg) (6).

For additional vapor pressure data, see Table 1 and Figure 3.

Latent Heat of Vaporization, ΔHv @ −103.7 °C ..... 13.558 kJ/mol; 3.240 kcal·mol

For additional ΔHv data, see Table 1.

Thermodynamic Properties of Ethylene As Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	42.886 J/(mol·°K)
Entropy, S°	219.225 J/(mol·°K)
Gibbs Energy Function, $(G^\circ_{298} - H^\circ_{298})/298$	−219.225 J/(mol·°K)
Enthalpy Difference, $H^\circ_{298} - H^\circ_0$	10.519 kJ/mol
Enthalpy of Formation, ΔH_f°	52.467 kJ/mol
Gibbs Energy of Formation, ΔG_f°	68.358 kJ/mol

Thermodynamic Data

For the thermodynamic properties of saturated ethylene, superheated ethylene vapor, and compressibility factors, see Tables 1, 2, and 3, respectively.

REFERENCES

[1] For extensive tabulations of the thermodynamic properties of ethylene, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] F. W. Patty, *Industrial Hygiene and Toxicology, 1949*, Volume II, p. 747, Interscience Publishers, Inc., New York, New York.

[3] **Chemical Engineers' Handbook**, 4th edition, R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, editors, *1963*, p. 3-53, McGraw-Hill Book Co., Inc., New York, New York.

[4] **Ibid.**, p. 3-60.

[5] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Rev. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[6] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[7] R. York, Jr., and E. F. White, Jr., *Trans. Amer. Inst. Chem. Engrs.* 40, 227-250 (1944).

[8] R. J. Walters, *et al.*, *Chem. Eng. Prog.* 50, 511-515 (1954).

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED ETHYLENE (7)

Temperature, °K	Vapor Pressure kPa	Vapor Pressure atm	Entropy J/(mol·°K) Liquid	Entropy J/(mol·°K) Vapor	Enthalpy kJ/mol Liquid	Enthalpy kJ/mol Vapor	Latent Heat of Vaporization kJ/mol	Specific Volume dm^3/kg Liquid	Specific Volume dm^3/kg Vapor	Density kg/dm^3 Liquid	Density kg/dm^3 Vapor
104.00	0.122	0.001 2	−33.170	120.195	−4.447	11.510	15.957		253 707		0.000 004
110.93	0.375	0.003 7	−27.596	114.092	−3.967	11.745	15.712		87 711		0.000 012
122.04	1.793	0.017 7	−22.149	103.293	−3.206	12.111	15.317		20 514		0.000 05
133.15	6.140	0.060 6	−16.221	95.898	−2.449	12.482	14.931		6 436		0.000 16
144.26	17.124	0.169	−10.821	90.029	−1.698	12.853	14.551		2 481		0.000 40
155.37	40.733	0.402	−5.845	85.334	−0.950	13.212	14.162		1 119		0.000 89
166.48	84.809	0.837	−1.209	81.226	−0.204	13.513	13.717		564.8		0.001 8
169.45	101.325	1.000	0.000	79.981	0.000	13.558	13.558	1.759	478.9	0.568 4	0.002 1
177.59	159.840	1.577	2.943	77.035	0.561	13.728	13.167	1.796	312.4	0.556 8	0.003 2
188.71	277.387	2.738	7.606	74.417	1.356	13.969	12.613	1.850	186.5	0.540 4	0.005 4
199.82	452.072	4.462	11.679	71.847	2.140	14.165	12.025	1.949	117.3	0.513 1	0.008 5
210.93	696.072	6.870	16.128	70.121	2.950	14.340	11.390	1.985	108.1	0.503 9	0.009 3
222.04	1 023.281	10.099	19.555	67.716	3.775	14.471	10.696	2.065	53.50	0.484 2	0.018 7
233.15	1 421.975	14.034	22.713	65.215	4.617	14.530	9.913	2.165	37.02	0.461 9	0.027 0
244.26	1 998.332	19.722	26.351	63.185	5.523	14.523	9.000	2.286	26.16	0.437 4	0.038 2
255.37	2 674.676	26.397	30.249	61.060	6.541	14.412	7.871	2.442	18.79	0.409 5	0.053 3
266.48	3 500.779	34.55	34.838	58.583	7.800	14.126	6.326	2.679	13.23	0.373 2	0.075 7
277.59	4 513.016	44.54	41.469	54.968	9.698	13.447	3.749	3.143	8.68	0.318 1	0.115 2
283.05	5 116.913	50.50	46.529	46.529	11.204	11.204	0.000	4.370	4.37	0.228 8	0.228 8

Table 2. THERMODYNAMIC PROPERTIES

H, ENTHALPY, kJ/mol; **S**, ENTROPY,

Pressure kPa	atm		177.59	188.71	199.82	210.93	222.04	233.15	244.26	255.37	266.48	277.59	288.71	299.82	310.93	Tem 322.04
101.325	1	H	13,838 7	14.236 5	14.627 7	15.038 6	15.449 5	15.866 8	16.297 3	16.734 2	17.177 7	17.634 2	18.110 2	18.586 3	19.081 9	19.590 6
		S	81.577	83.808	85.920	87.798	89.677	91.555	93.316	95.076	96.836	98.480	100.123	101.767	103.409	104.936
		V	503.2	537.9	572.3	606.4	640.3	673.8	707.2	740.5	780.2	806.8	839.8	872.7	905.8	938.9
202.650	2	H		14.079 9	14.497 3	14.927 7	15.351 6	15.782 1	16.279 0	16.669 0	17.119 0	17.575 5	18.058 1	18.534 1	19.036 3	19.545 0
		S		77.352	79.465	81.343	83.338	85.216	86.977	88.738	90.498	92.141	93.785	95.545	97.189	98.715
		V		261.6	279.6	297.5	315.1	332.4	349.5	366.6	383.6	400.4	417.2	433.9	450.5	467.2
405.300	4	H			14.229 9	14.706 0	15.156 0	15.606 0	16.062 5	16.525 5	16.995 1	17.464 6	17.953 7	18.442 8	18.951 5	19.473 2
		S			73.126	75.239	77.234	79.230	81.108	82.869	84.746	86.507	88.151	89.794	91.555	93.081
		V			133.0	142.8	152.3	161.6	170.6	179.7	188.5	197.2	205.8	214.4	222.9	231.4
607.950	6	H				14.451 7	14.940 8	15.429 9	15.960 0	16.382 0	16.864 6	17.347 2	17.849 4	18.351 5	18.866 7	19.388 5
		S				71.248	73.361	75.357	77.352	79.230	81.108	82.869	84.629	86.272	88.033	89.559
		V				90.90	97.76	104.4	110.9	114.4	117.2	131.0	135.3	141.3	147.1	152.8
1 013.250	10	H					14.503 8	15.051 7	15.573 4	16.082 1	16.590 7	17.112 5	17.634 2	18.155 9	18.684 1	19.225 4
		S					67.845	70.309	72.305	74.182	76.178	78.056	79.817	81.695	83.455	84.981
		V					53.69	58.43	62.80	67.05	71.17	75.04	78.91	82.65	86.28	91.02
2 026.500	20	H								15.162 5	15.814 7	16.440 7	17.040 7	17.621 1	18.208 1	18.788 5
		S								65.731	68.314	69.371	72.539	74.535	76.413	78.174
		V								28.66	31.40	34.02	36.39	38.52	40.70	42.76
4 053.000	40	H										14.419 1	15.475 5	16.316 8	17.105 9	17.803 7
		S										59.040	62.680	65.497	68.079	70.192
		V										11.99	14.23	15.92	17.42	18.85
6 079.500	60	H											11.151 8	14.171 3	15.579 9	16.545 1
		S											45.777	55.402	60.684	63.971
		V											4.306	7.115	8.990	10.61
8 016.000	80	H											9.547 5	11.497 4	13.369 1	14.888 6
		S											39.908	46.247	55.990	57.281
		V											3.177	4.057	5.119	6.431
10 132.500	100	H											9.358 4	10.519 2	11.901 8	13.480 0
		S											38.382	42.608	47.068	51.763
		V											2.750	3.122	3.559	4.306
15 198.750	150	H											9.071 4	9.977 9	10.936 6	11.967 0
		S											36.152	39.204	42.374	45.543
		V											2.427	2.684	2.872	3.122
20 265.000	200	H											9.019 3	9.841 0	10.682 2	11.549 6
		S											34.627	37.326	40.143	42.960
		V											2.310	2.435	2.622	2.747
25 331.250	250	H											9.012 7	9.769 2	10.551 8	11.367 0
		S											33.570	36.270	38.852	41.434
		V											2.185	2.310	2.435	2.622
30 397.500	300	H											8.993 2	9.750 0	10.525 7	11.327 9
		S											32.513	35.213	37.796	40.143
		V											2.123	2.247	2.372	2.435

OF SUPERHEATED ETHYLENE (7)

J(mol·°K); **V**, SPECIFIC VOLUME, dm^3/kg

perature, °K 333.15	344.26	355.37	366.48	377.59	388.71	399.82	410.93	422.04	433.15	444.26	455.37	466.48	477.59	488.70	499.82
20.105 8	20.634 1	21.181 9	21.742 7	22.303 6	22.884 0	23.477 5	24.083 9	24.703 5	25.329 6	25.975 2	26.620 8	27.286 0	27.964 2	28.655 5	29.372 9
106.579	108.105	109.631	111.275	112.800	114.325	115.735	117.260	118.786	120.312	121.721	123.246	124.656	126.064	127.473	128.881
971.4	1 004	1 037	1 070	1 102	1 136	1 168	1 200	1 234	1 266	1 299	1 332	1 364	1 397	1 430	1 462
20.060 2	20.594 9	21.142 7	21.710 1	22.271 0	22.857 9	23.457 9	24.064 4	24.683 9	25.310 0	25.962 2	26.607 8	27.273 0	27.951 2	28.642 5	29.359 9
100.358	101.884	103.410	105.053	106.697	108.223	109.631	111.157	112.683	114.325	115.735	117.260	118.669	120.078	121.486	123.017
483.8	500.4	516.9	533.4	549.9	566.2	583.1	599.3	615.9	631.8	648.6	664.9	681.1	697.3	714.2	730.4
19.995 0	20.529 7	21.084 1	21.651 4	22.212 3	22.805 7	23.405 7	24.012 2	24.638 3	25.264 3	25.916 5	26.568 6	27.233 8	27.912 1	28.609 9	29.327 2
94.724	96.250	97.776	99.418	100.944	102.470	103.996	105.522	107.048	108.574	109.983	111.626	113.034	114.443	115.851	117.377
239.9	248.3	256.8	265.1	273.4	281.8	290.1	298.5	306.7	315.0	323.3	331.6	339.8	348.0	356.2	364.5
19.916 7	20.458 0	21.018 8	21.586 2	22.160 1	22.747 0	23.353 5	23.966 6	24.592 6	25.225 2	25.870 8	26.523 0	27.194 7	27.873 0	28.570 8	29.294 6
91.203	92.846	94.372	96.015	97.541	99.067	100.476	102.119	103.645	105.171	106.697	108.223	109.631	111.040	112.448	113.974
158.6	164.4	170.1	175.7	181.4	186.9	192.5	198.1	203.7	209.3	214.9	220.4	226.0	231.1	237.0	242.5
19.766 7	20.321 0	20.888 4	21.468 8	22.042 7	22.642 7	23.249 2	23.868 7	24.501 3	25.133 9	25.792 6	26.444 7	27.116 5	27.807 7	28.505 5	29.229 4
86.742	88.386	89.912	91.672	93.198	94.842	96.250	97.776	99.418	100.944	102.353	103.879	105.405	106.813	108.223	109.631
93.58	97.14	100.7	104.1	107.6	111.1	114.5	117.9	121.4	124.8	128.2	131.6	134.9	138.3	141.6	145.0
19.362 4	19.949 3	20.549 3	21.149 3	21.749 2	22.368 8	22.994 9	23.627 4	24.266 6	24.918 7	25.583 9	26.249 1	26.933 8	27.625 1	28.336 0	29.066 4
80.051	81.695	83.338	85.216	86.860	88.386	89.912	91.555	93.197	94.724	96.250	97.776	99.185	100.710	102.119	103.527
44.76	46.70	48.57	50.44	52.31	54.19	56.00	57.81	59.56	61.37	63.18	64.92	66.67	68.42	70.11	71.85
18.482 0	19.140 6	19.805 8	20.464 5	21.116 7	21.775 3	22.440 5	23.112 2	23.784 0	24.462 2	25.160 0	25.851 3	26.555 6	27.273.0	27.996 9	28.746 8
72.422	74.417	76.296	78.174	79.934	81.577	83.220	84.864	86.507	88.151	89.677	91.320	92.846	94.254	95.780	97.189
20.16	21.29	22.41	23.60	24.66	25.72	26.72	27.78	28.78	29.71	30.65	31.59	32.52	33.52	34.40	35.27
17.438 5	18.227 6	18.990 6	19.734 1	20.451 5	21.162 3	21.873 2	22.571 0	23.275 3	23.986 1	24.710 0	25.433 9	26 177 4	26.907 8	27.651 2	28.420 8
66.670	69.018	71.248	73.244	75.122	77.000	78.760	80.638	82.282	84.043	85.569	87.212	88.738	90.264	91.790	93.316
11.61	12.80	13.67	14.61	15.48	16.23	17.04	17.79	18.48	19.17	19.85	20.91	21.23	21.85	22.54	23.16
16.192 9	17.177 7	18.103 7	18.945 0	19.747 1	20.523 2	21.286 2	22.023 2	22.766 6	23.510 1	24.266 6	25.016 5	25.779 5	26.542 6	27.312 1	28.094 7
61.271	64.323	66.788	69.136	71.365	73.361	75.240	77.117	78.878	80.756	82.399	84.160	85.804	87.329	88.855	90.380
7.553	8.551	9.364	10.18	10.86	11.55	12.17	12.80	13.42	13.98	14.55	15.05	15.61	16.10	16.79	17.17
14.888 6	16.075 5	17.151 6	18.116 8	18.997 2	19.851 5	20.679 7	21.468 8	22.264 4	23.040 5	23.829 6	24.612 2	25.407 8	26.255 6	26.973 0	27.781 7
56.341	59.745	62.797	65.614	67.962	70.192	72.070	74.182	76.061	78.056	79.753	81.577	83.220	84.864	86.507	88.151
5.119	6.056	6.805	7.553	8.177	8.801	9.304	9.863	10.36	10.86	11.36	11.86	12.30	12.80	13.17	13.67
13.030 0	14.171 3	15.325 6	16.408 1	17.425 5	18.397 2	19.336 3	20.203 7	21.090 6	21.944 9	22.812 3	23.666 6	24.520 9	25.362 2	26.196 9	27.051 2
48.946	52.350	55.637	58.689	61.506	63.971	66.201	68.431	70.544	72.656	74.652	76.530	78.409	80.169	81.812	83.573
3.496	3.871	4.181	4.620	5.058	5.432	5.867	6.242	6.616	6.930	7.303	7.678	7.99	8.30	8.616	8.926
12.462 6	13.440 8	14.445 2	15.462 5	16.453 8	17.425 5	18.371 1	19.277 6	20.197 1	21.090 6	21.997 1	22.884 0	23.784 0	24.651 3	25.479 6	26.405 6
46.012	48.829	51.646	54.464	57.163	59.745	62.092	64.323	66.553	68.666	70.662	72.774	74.652	76.530	78.291	80.051
2.934	3.122	3.371	3.559	3.871	4.121	4.370	4.680	4.930	5.308	5.557	5.807	6.056	6.306	6.555	6.741
12.227 8	13.108 2	14.027 8	14.979 9	15.906 0	16.832 0	17.758 1	18.664 6	19.584 2	20.484 1	21.194 9	22.297 1	23.204 3	24.097 0	24.990 4	25.896 9
44.134	46.717	49.181	51.763	54.229	56.693	59.040	61.389	63.613	65.849	67.845	69.957	71.835	73.714	75.591	77.352
2.684	2.872	3.059	3.184	3.371	3.559	3.682	3.871	4.121	4.306	4.431	4.680	4.869	5.055	5.244	5.493
12.149 6	12.977 8	13.832 1	14.693 0	15.566 9	16.447 3	17.340 7	18.253 7	19.173 3	20.066 7	20.777 5	21.873 2	22.786 2	23.686 1	24.592 6	25.512 2
42.725	45.073	47.420	50.003	52.351	54.698	56.811	59.158	61.389	63.501	65.497	67.610	69.605	71.483	73.244	75.122
2.559	2.684	2.809	2.934	3.059	3.184	3.371	3.496	3.622	3.807	3.996	4.121	4.306	4.431	4.620	4.805

Table 3. COMPRESSIBILITY FACTORS FOR ETHYLENE (8)

Pressure		Temperature, °K						
kPa	atm	244.26	255.37	266.48	277.59	288.70	299.82	310.93
344.7	3.402	0.961 3	0.966 9	0.971 2	0.974 3	0.977 2	0.979 8	0.982 2
689.4	6.804	0.921 4	0.932 3	0.940 6	0.947 8	0.953 9	0.959 3	0.963 7
1 034.2	10.207	0.878 9	0.896 0	0.909 3	0.920 2	0.930 1	0.938 4	0.945 1
1 378.9	13.609	0.833 2	0.857 2	0.877 0	0.892 5	0.906 1	0.917 2	0.926 2
1 723.7	17.011		0.816 1	0.842 8	0.863 8	0.881 2	0.895 6	0.907 5
2 068.4	20.414		0.771 6	0.805 4	0.833 6	0.855 8	0.873 8	0.888 9
2 413.1	23.816			0.765 3	0.800 7	0.828 1	0.850 4	0.869 4
2 757.9	27.218				0.765 4	0.799 5	0.826 7	0.849 4
3 102.6	30.620				0.726 5	0.768 9	0.801 3	0.828 2
3 447.4	34.023				0.683 5	0.736 5	0.775 5	0.806 5
3 792.1	37.425				0.633 6	0.701 6	0.748 2	0.783 9
4 136.8	40.827					0.663 1	0.719 1	0.760 5

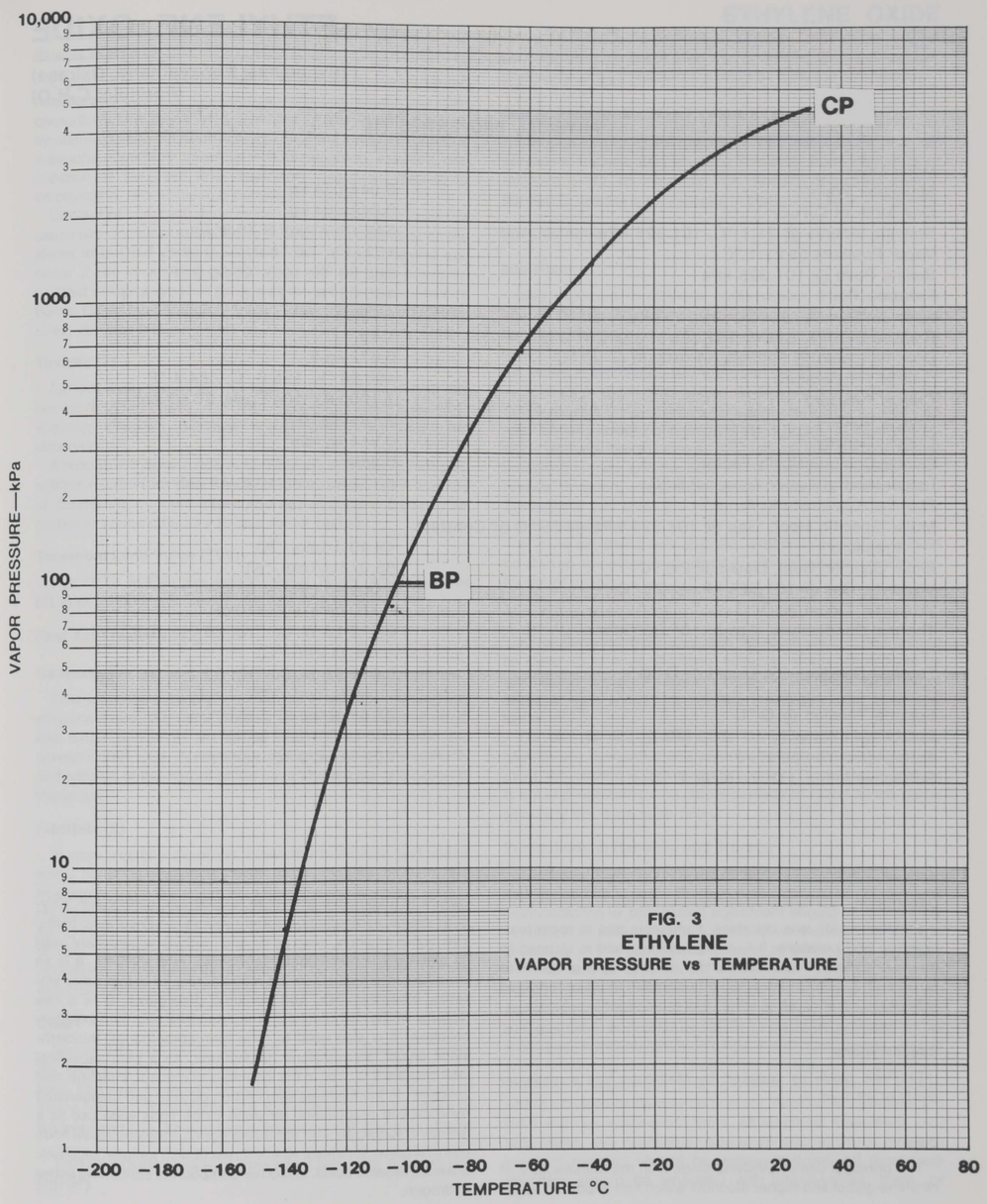


FIG. 3
ETHYLENE
VAPOR PRESSURE vs TEMPERATURE

ETHYLENE OXIDE

(Synonyms: Epoxyethane; Oxirane)
(Formula: C_2H_4O)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.044 054 kg
One Mole of C_2H_4O	0.044 054 kg
Specific Volume @ 21.1 °C, 101.325 kPa	548.1 dm^3/kg; 8.78 ft^3/lb
Vapor Pressure @ 21.1 °C	152 kPa; 1.52 bar; 22.0 psia; 1.50 atm
Boiling Point @ 101.325 kPa	283.66 °K; 10.5 °C; 50.9 °F
Freezing Point	160.65 °K; −112.5 °C; −170.5 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	1.795 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	1.49
Density, Liquid @ Saturation Pressure @ 20 °C	0.872 kg/l
Critical Temperature	468.95 °K; 195.8 °C; 384.4 °F
Critical Pressure	7 190 kPa; 1043 psia; 70.97 atm
Critical Volume	3.185 dm^3/kg
Critical Density	0.314 kg/dm^3
Critical Compressibility Factor	0.259
Latent Heat of Fusion @ −112.5 °C	5.173 kJ/mol; 1236.42 cal/mol
Flammability Limits In Air	3.0-80.0 % (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	49.40 J/(mol·°K)
Molar Specific Heat, Liquid @ 2.5 °C	86.078 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.009 45 mPa·s; 0.009 45 cP
Viscosity, Liquid @ O °C	0.310 mPa·s; 0.310 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.012 13 W/(m·°K); 29.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ O °C	0.038 97 W/(m·°K); 93.1 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ O °C	27.5 mN/m; 27.5 dyn/cm
Solubility In Water @ 101.325 kPa @ 20 °C	195 cm^3/1 cm^3 water
Autoignition Temperature	702 °K; 429 °C; 804 °F
Refractive Index, Liquid, n_D @ 7 °C	1.359 7

Description

Ethylene oxide is a colorless, flammable gas at room temperature and pressure. It is easily liquefied and is shipped in drums or cylinders as a liquid under its own vapor pressure of 50 kPa (7.3 psig) at 21.1 °C. It is miscible in all proportions with water, alcohol, ethyl ether, and most organic solvents.

Specifications

Ethylene oxide as supplied by Matheson has a minimum purity of 99.7 wt. %.

Uses

The principal use of ethylene oxide is in the manufacture of ethylene glycol and higher alcohols which find important applications in automotive antifreeze, explosives, cellophane, polyester resins, synthetic fibers and rubbers, and hydraulic fluids. The higher alcohols, such as di- and triethylene glycol are used as plasticizers, humectants, lubricants, and solvents. It is an important intermediate in the manufacture of glycol ether solvents, ethanolamines, and nonionic detergents. It is a raw material in the manufacture of acrylonitrile and hydroxyethylcellulose. It is also used to form mercaptoethanol, thiodiethylene glycol, and ethylene halohydrins. As a pharmaceutical intermediate it is used in the synthesis of choline, thiamine, and procaine. In the mixtures with carbon dioxide and halogenated hydrocarbon propellants, ethylene oxide finds wide use as a fumigant, fungicide, and sterilizing agent. Ethylene oxide finds use in organic synthesis where it reacts with amines, alcohols, phenols, organic acids, and other compounds containing active hydrogen.

Effects in Man (2)

Exposure to low concentrations of vapor will cause delayed nausea and vomiting. Continuous exposure to even low concentrations will result in a numbing of the sense of smell. Inhalation of high concentrations of ethylene oxide can produce a general anesthetic effect as well as coughing, vomiting, and irritation of the eyes and respiratory passages, leading to emphysema, bronchitis and pulmonary edema.

Contact of liquid ethylene oxide with exposed skin does not cause skin irritation immediately, but when spilled in or on the shoes or on the clothing, delayed skin burns (blisters) can occur if the shoes and clothing are not removed promptly. Contact of liquid ethylene oxide with the eyes can cause severe burns. Rapid evaporation of the liquid on the skin produces an effect like frostbite.

Toxicity (2)

Serious systemic poisoning from ethylene oxide in man has been rare. A few cases have been reported, in which headache, vomiting, dyspnea, diarrhea, and lymphocytosis have been observed.

Although ethylene oxide is considered to be an irritant gas, neither irritation nor odor can be relied upon to provide warning of dangerous concentrations of vapor. Ethylene oxide is reported to cause olfactory fatigue rather rapidly.

Threshold Limit Value (TLV)

The 1979 ACGIH has established a Threshold Limit Value (TLV) of 50 ppm (90 mg/m^3) for ethylene oxide.*

First Aid Treatment (2)

General

First aid should be started at once in case of contact with ethylene oxide. Workers showing symptoms or signs of ethylene oxide poisoning should be removed at once from the contaminated area. A physician should be called immediately and notified of the nature of the case and the exact location of the victim.

Frostbite (2)

In case frostbite develops, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Eyes

Should ethylene oxide, as liquid or vapor, contact the eyes, the eyes should be irrigated copiously with water for 15 minutes. The eyelids should be held apart during the irrigation to insure contact of the water with all the tissues of the surface of the eyes and lids. Should eye irritation persist, the eyes should be irrigated for a second 15 minute period, and a physician, preferably an eye specialist, should be called in attendance.

* 1979 ACGIH Notice of Intent to Change to 10 ppm (20 mg/m^3).

Suggestions for Medical Treatment (2)

Through unpublished reports, it has been found that for persistent nausea and vomiting resulting from inhalation of ethylene oxide, an intramuscular injection of sodium phenobarbital (2 grains) is very helpful in controlling such symptoms.

Specific Actions

Inhalation

Mild exposure to ethylene oxide vapors at times produce nausea and vomiting. Persons showing such symptoms should be placed in bed and given warm water in sufficient amounts to aid in washing out their stomachs. In severe exposures, if the victim is breathing, 100% oxygen should be administered as soon as possible after exposure. The victim should breathe 100% oxygen under positive exhalation pressure for one-half hour periods every hour for at least 3 hours. If there are no signs of lung congestion at the end of this period, and if breathing is easy and the color of the skin and mucous membranes is good, oxygen inhalation may be discontinued. Throughout this time, the victim should be kept comfortably warm, but not hot.

In case breathing has stopped, artificial respiration should be started immediately, preferably with simultaneous administration of oxygen.

Skin Contact

All clothing contaminated with liquid ethylene oxide should be removed at once. Clothing, including shoes, should not be worn again. Shoes can seldom be decontaminated. All affected areas of skin should be washed thoroughly with soap and water.

For skin burns resulting in the formation of blisters, if the blisters are evacuated and solid petroleum dressings are applied, the healing is usually quite prompt. The blister formation is out of proportion to the actual damage to tissue as the burns generally are quite superficial.

Precautions in Handling and Storage

The hazards in handling ethylene oxide are due to its flammability and its toxicity. Storage areas and buildings to house manufacturing or processing equipment should be adequately ventilated to prevent accumulation of ethylene oxide vapors. Breathing of the vapors and contact of either liquid or vapor with the skin or eyes should be avoided. Approved personal protective equipment (gas-tight chemical safety goggles, rubber gloves and apron, rubber shoes or boots, full-faced industrial gas mask approved by NIOSH) should be provided for all individuals handling ethylene oxide. Keep heat, flames, and all spark-producing devices away from storage areas, pipelines, processing equipment, and cylinders, and from all places where ethylene oxide may be present. Ground all cylinders and lines and use spark-proof tools. All electrical equipment, motors, lights, and flashlights used in an area in which ethylene oxide is handled should be explosion-proof. All lines from cylinders should be equipped with check-valves, traps, or

vacuum breaks to prevent suckback into the cylinder to avoid the possibility of undesirable reactions, which might cause a violent reaction within the cylinder. Ethylene oxide may rearrange chemically and/or polymerize violently when in contact with highly active catalytic surfaces such as anhydrous iron, tin, and aluminum chlorides; pure iron and aluminum oxides; and alkali metal hydroxides.

Caution

Ethylene oxide may polymerize on prolonged storage despite an additive which Matheson incorporates to minimize the problem. We recommend using the product within 90 days of the filling date indicated on our tag. Refrigerated storage will prolong shelf life.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Equipment to contain ethylene oxide should be pressure-tested with nitrogen and be leak-proof prior to use with ethylene oxide.

Analytical Detection

Matheson has available a manually operated "Toxic Gas Detector" Model 8014K which provides accurate, dependable, and reproducible results in determining concentrations of ethylene oxide in the range of 5–100 ppm using the Model 122SB detector tube. A color stain is produced in the detector tube. The stain varies in length according to the concentration of ethylene oxide present; the length, and hence concentration, is read directly from the tube.

Materials of Construction

All equipment and piping to handle ethylene oxide should be constructed of steel and properly grounded. Do not use copper, silver, magnesium, and their alloys as materials of construction. All piping and equipment to contain ethylene oxide should be designed to have a working pressure of at least 340 kPa (50 psig) with a safety factor conforming to the ASME code. Shut-off valves and control valves should be of steel or stainless steel designed for working pressures of 1 030 kPa (150 psig) or over. Mercury-filled instruments should be provided with mercury traps and an inert gas purge which is free of acetylene and carbon dioxide. All-welded construction is preferred to riveted construction. Garlock No. 7021 or the equivalent has been found to be a satisfactory material for gaskets. Either reciprocating or centrifugal pumps may be used. If the reciprocating type is used, the nonlubricated liquid end should have a cast iron or steel cylinder with a liner, piston, and rings of cast iron; the valves and rods should be 18-8 stainless steel. Good performance has been obtained with Garlock No. 530 chevron packing or its equivalent.

All process equipment should be protected with relief valves and/or rupture diaphragms. All vent lines should extend to a safe area outside the building, and manual vents equipped with flame arresters.

Cylinder and Valve Description

Ethylene oxide is shipped in DOT approved, insulated steel drums containing 400 lbs net, and in DOT approved, low pressure steel cylinders. Cylinder valves and their outlet connections are constructed of steel. The outlet connection designated as standard by the Compressed Gas Association (CGA) is No. 510. This has a thread size of 0.885 inch diameter with left-hand internal threads accepting a bullet-shaped nipple. (See Figure 1 for an illustration of the valve outlet and its mating

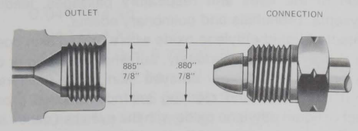


Fig. 1. CONNECTION 510 .885"-14 LH INT. accepting a Bullet Shaped Nipple

connection.) Lecture bottles have a special 5/16 inch-32 threads per inch, female valve outlet.

Drums are equipped with straight dip tubes which extend to the bottom of the drum for removal of liquid ethylene oxide while the drum is in normal position, by pressurization with an inert gas such as nitrogen to about 340 kPa (50 psig). Cylinders of 10 lb or more are equipped with goose neck dip tubes for removal of liquid, when the cylinder is placed in a horizontal position with the valve outlet facing upwards.

If the user requires ethylene oxide vapor from drums, it will be necessary to provide a vaporizer of adequate design. A water bath heated to a maximum of 50 °C (122 °F) may be used to empty small cylinders by increasing the vapor pressure of ethylene oxide.

Safety Devices

Cylinders of ethylene oxide are equipped with safety devices of fusible metal plugs, melting at about 73.9 °C (165 °F).

Drums have 4 fusible metal plugs as safety devices. In addition, each drum has a vapor valve which is equipped with a spring-loaded pressure relief valve set at 450 kPa (65 psig). This valve is effective only during loading or unloading and is intended to prevent overpressurizing the drum with an inert gas.

Recommended Controls

Manual Controls

For manual flow control, Matheson supplies a 303 stainless steel needle valve, Model 61-510, for direct attachment to the cylinder valve outlet. This valve can be obtained with a serrated hose end, ¼" compression fitting, or ¼" NPT male or female pipe outlet.

Manual needle valve Model 325 is recommended for use with lecture bottles.

Shipping Regulations

Ethylene oxide is classified by the DOT as a flammable liquid and is shipped with the required "Red Label."

Commercial Preparation

Ethylene oxide is usually made by direct oxidation of ethylene by oxygen at high temperature in the presence of silver catalysts.

It is also produced in lesser amounts of the chlorohydrin process, which involves conversion of ethylene in ethylene chlorohydrin followed by conversion into ethylene oxide, using a milk-of-lime slurry or a solution of sodium hydroxide.

Chemical Properties

(a) Ethylene oxide reacts with water forming glycol or a polyglycol.

(b) With halogen hydrides, ethylene oxide gives halohydrins.

(c) With hydrogen cyanide, ethylene oxide gives ethylene cyanohydrin.

(d) With alcohols, ethylene oxide forms hydroxy ethers and monoethers of polyglycols.

(e) With aldehydes and ketones, ethylene oxide forms cyclic acetals and cylic ketals, respectively.

(f) Ethylene oxide reacts with carboxylic acids forming hydroxy esters.

(g) With ammonia, ethylene oxide gives mono-, di-, and triethanolamines and morpholine.

(h) Ethylene oxide reacts with the methylene groups in malonic and acetoacetic esters to give lactones.

(i) With sodium acetylides, ethylene oxide gives acetylenic alcohols.

(j) With hydrogen sulfide, ethylene oxide gives thiodiglycol and 2-mercaptoethanol, the proportions of each compound depending on the reaction conditions.

(k) With sodium bisulfite, ethylene oxide forms a hydroxy sulfonic acid.

(l) With Grignard reagents, ethylene oxide gives primary alcohols, lengthening the chain by 2 carbon atoms, as well as other by-products.

(m) Thermal decomposition gives ketene, acetaldehyde, carbon monoxide, ethane, propane, methane, and hydrogen.

(n) Ethylene oxide reacts with potassium thiocyanate or thiourea in aqueous solution to give ethylene sulfide.

(o) Phosgene reacts with ethylene oxide to give 2-chloroethyl chloroformate $ClCH_2CH_2OCOCl$.

(p) Ethylene oxide reacts with phosphorus oxychloride in the presence of aluminum chloride to give tris (2-chloroethyl) phosphate $OP(OCH_2CH_2Cl)_3$, a valuable plasticizer.

(q) Ethylene oxide reacts with acyl halides in the presence of hydrogen chloride as catalyst to give 2-haloethyl esters. E.g., acetyl chloride yields 2-chloroethyl acetate.

Thermodynamic and Detailed Physical Data

Molecular Structure

Ethylene oxide is a highly strained three-membered cyclic ether and opens readily under mild (acidic) conditions.

Ethylene oxide has C_{2v} symmetry and a symmetry number of two. The atomic parameters are (1): bond distances: C-H 1.080 2 Å (1.080 2 × 10^{-10} m), C-O 1.436 3 Å (1.436 3 × 10^{-10} m), C-C 1.427 8 Å (1.427 8 × 10^{-10} m); bond angles: H-C-H 116.85°, H_2-C-C 158.08°, H_2-C-O 142.76°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous ethylene oxide.

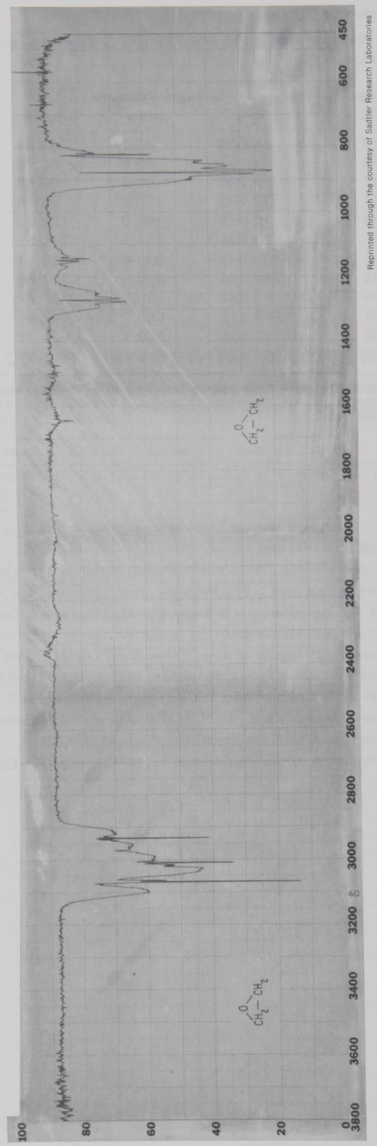


Fig. 2. Infrared spectrum of gaseous ethylene oxide over the frequency region of 3 800 cm^{-1} to 450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure (complete scan): 5.33 kPa (40 mmHg) (5).

Vapor Pressure (3)

Vapor pressure data up to 101.325 kPa (760 mmHg) are shown below:

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
223.79	4.523	45.2	33.94
229.85	6.759	67.6	50.70
234.92	9.290	92.9	69.68
239.89	12.495	125.0	93.73
244.99	16.656	166.6	124.93
251.31	23.408	234.1	175.58
258.33	33.349	333.5	250.14
263.33	42.354	423.5	317.68
268.26	53.032	530.3	397.77
273.35	66.315	663.2	497.41
278.80	83.336	833.4	625.07
283.66	101.325	1 013.25	760.00

For vapor pressure data above 101.325 kPa (1 atm), see Table 1 and Figure 3 (vapor pressure curve).

Latent Heat of Vaporization, △Hv

Temperature, °C	△Hv, kJ/mol
0	26.063
10.5	25.527
20	25.021

For △Hv data at other temperatures, see Table 1.

Thermodynamic Properties of Ethylene Oxide As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	47.903 J/(mol·°K)
Entropy, S°	242.906 J/(mol·°K)
Gibbs Energy Function, $(G_{298}^\circ - H_{298}^\circ)/298$	−242.906 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	10.862 kJ/mol
Enthalpy of Formation, $\triangle H_f^\circ$	−52.635 kJ/mol
Gibbs Energy of Formation, $\triangle G_f^\circ$	−13.238 kJ/mol

For the thermodynamic properties of saturated ethylene oxide and superheated vapor, see Tables 1 and 2, respectively.

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of ethylene oxide, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 43–47, Matheson, Lyndhurst, New Jersey.

[3] W. F. Giaque and J. Gordan, *J. Amer. Chem. Soc.* 71, 2176 (1949).

[4] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[5] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[6] C. J. Walters and J. M. Smith, *Chem. Eng. Progr.* 48, 337 (1952).

[7] National Fire Protection Association, Vol. 14, 1976, National Fire Codes, *NFPA Manual of Hazardous Chemical Reactions*, pp. 491M-132–133, 491M-172.

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED ETHYLENE OXIDE (6)

Temperature, °K	Pressure kPa	atm	Entropy J/(Mol·°K) Liquid	Vapor	Enthalpy kJ/mol Liquid	Vapor	Latent Heat of Vaporization kJ/Mol	Specific Volume DM^3/KG Liquid	Vapor	Density KG/DM^3 Liquid	Vapor
294.26	151.683	1.497	0.000	84.659	0.000	24.916	24.916	1.136 2	341.2	0.880 2	0.002 9
310.93	266.079	2.626	4.756	81.820	1.454	25.418	23.964	1.162 4	200.5	0.860 2	0.004 9
327.59	438.129	4.324	9.548	79.664	2.980	25.951	22.971	1.196 1	125.2	0.836 0	0.008 0
344.26	687.389	6.784	14.395	78.042	4.598	26.513	21.915	1.239 2	81.53	0.807 0	0.012 3
360.93	1 034.2	10.207	19.335	76.935	6.329	27.128	20.799	1.289 7	54.94	0.775 3	0.018 2
377.59	1 501.6	14.820	24.275	76.125	8.203	27.783	19.580	1.348 4	38.02	0.741 6	0.026 3
394.26	2 111.8	20.842	29.362	75.442	10.251	28.418	18.167	1.416 5	26.68	0.706 0	0.037 5
410.93	2 889.6	28.518	34.819	74.650	12.525	28.859	16.334	1.498 2	18.85	0.667 5	0.053 0
427.59	3 857.5	38.071	40.735	74.042	15.034	29.278	14.244	1.610 6	13.37	0.620 9	0.074 8
444.26	5 040.0	49.741	46.947	73.047	17.799	29.381	11.582	1.779 2	9.40	0.562 0	0.106 4
460.93	6 458.2	63.738	53.637	71.388	20.861	29.033	8.172	2.060 1	6.41	0.485 4	0.156 0
468.93	7 191.2	70.972	64.144	64.144	26.319	26.319	0.000	3.183 8	3.183 8	0.314 1	0.314 1

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED ETHYLENE OXIDE (6)

H, ENTHALPY, KJ/MOL; **S**, ENTROPY, J/(MOL·°K); **V**, SPECIFIC VOLUME, DM^3/KG

Pressure kPa	Pressure atm		Temperature, °K 294.26	310.93	360.93	377.59	394.26	410.93	427.59	444.26	460.93	477.59
6.890	0.068	H	25.848	26.667	29.330	30.293	31.286	32.340	33.427	34.594	35.700	36.877
		S	113.136	115.827	123.772	126.371	128.970	131.587	134.186	136.785	139.347	141.983
		V	8 034	8 496	9 870	10.325	10 787	11 243	11 699	12 155	12 610	13 066
34,450	0.340	H	25.725	26.575	29.289	30.262	31.265	32.320	33.406	34.573	36.679	36.857
		S	99.404	102.207	110.316	112.933	115.552	118.150	120.767	123.366	125.947	128.583
		V	1 593	1 688	1 875	2 059	2 152	2 244	2 335	2 427	2 518	2 609
101.325	1.000	H	25.346	26.308	29.196	30.190	31.204	32.269	33.355	34.532	35.648	36.836
		S	89.359	92.529	101.174	103.846	106.483	109.100	111.736	114.353	116.934	119.606
		V	526.5	563.8	663.6	696.1	734.1	759.1	790.9	822.2	853.4	884.0
137.093	1.361	H	25.049	26.125	29.145	30.149	31.173	32.228	33.324	34.512	35.628	36.816
		S	85.930	89.470	98.501	101.211	103.865	106.667	109.118	111.736	114.353	117.026
		V	378.7	409.4	494.0	509.2	532.8	556.2	579.6	602.7	625.5	648.6
206.804	2.041	H		25.787	29.044	30.078	31.012	32.176	33.273	34.471	35.597	36.785
		S		84.935	94.925	97.709	100.382	103.017	105.671	108.325	110.943	113.634
		V		265.5	320.9	337.0	352.9	368.8	384.5	400.1	415.5	430.9
275.807	2.722	H			28.941	29.996	31.040	32.116	33.181	34.420	35.556	36.754
		S			92.290	95.165	97.874	100.529	103.202	105.874	108.491	111.202
		V			238.5	250.8	262.9	275.0	287.0	298.7	310.5	321.9
413.710	4.083	H			28.716	29.842	30.927	31.993	33.122	34.338	35.464	36.713
		S			88.419	91.479	94.262	96.953	99.662	102.372	105.027	107.736
		V			156.2	164.7	173.0	181.2	189.4	197.4	205.3	213.0
551.613	5.444	H			28.449	29.668	30.773	31.880	33.017	34.245	35.402	36.662
		S			85.452	88.769	91.644	94.354	97.101	99.847	102.538	105.321
		V			114.9	121.5	128.0	134.3	140.6	146.7	152.7	158.5
689.415	6.804	H			28.142	29.493	30.630	31.757	32.914	34.153	35.331	36.591
		S			82.907	86.557	89.543	92.327	95.110	97.874	100.603	103.368
		V			89.77	95.64	100.9	106.1	111.3	116.3	123.9	125.9
1 034.224	10.207	H			27.128	28.931	30.262	31.440	32.648	33.928	35.146	36.448
		S			76.935	82.023	85.507	88.401	91.313	94.188	97.008	99.773
		V			54.94	59.83	64.74	68.48	72.23	75.72	79.03	82.15
1 378.932	13.609	H				28.111	29.801	31.081	32.371	33.702	34.963	36.304
		S				77.784	82.226	85.396	88.474	91.461	94.373	97.248
		V				42.81	46.41	49.59	52.62	55.37	57.99	60.37
2 068.448	20.414	H					28.521	30.231	31.757	33.222	34.584	36.007
		S					75.848	80.438	84.106	87.386	90.501	93.561
		V					27.48	30.38	32.83	34.98	36.83	38.52
2 757.864	27.218	H						29.033	31.030	32.812	34.184	35.700
		S						75.590	80.456	84.437	87.589	90.797
		V						20.28	22.74	24.66	26.22	27.59
3 447.360	34.023	H							29.975	32.158	33.733	35.382
		S							76.623	81.525	85.120	88.714
		V							16.29	18.33	19.73	20.91
4 826.312	47.632	H								29.832	32.617	34.748
		S								74.374	80.641	85.157
		V								10.38	12.05	13.23
6 205.254	61.241	H									30.651	34.102
		S									75.130	82.484
		V									7.30	8.74

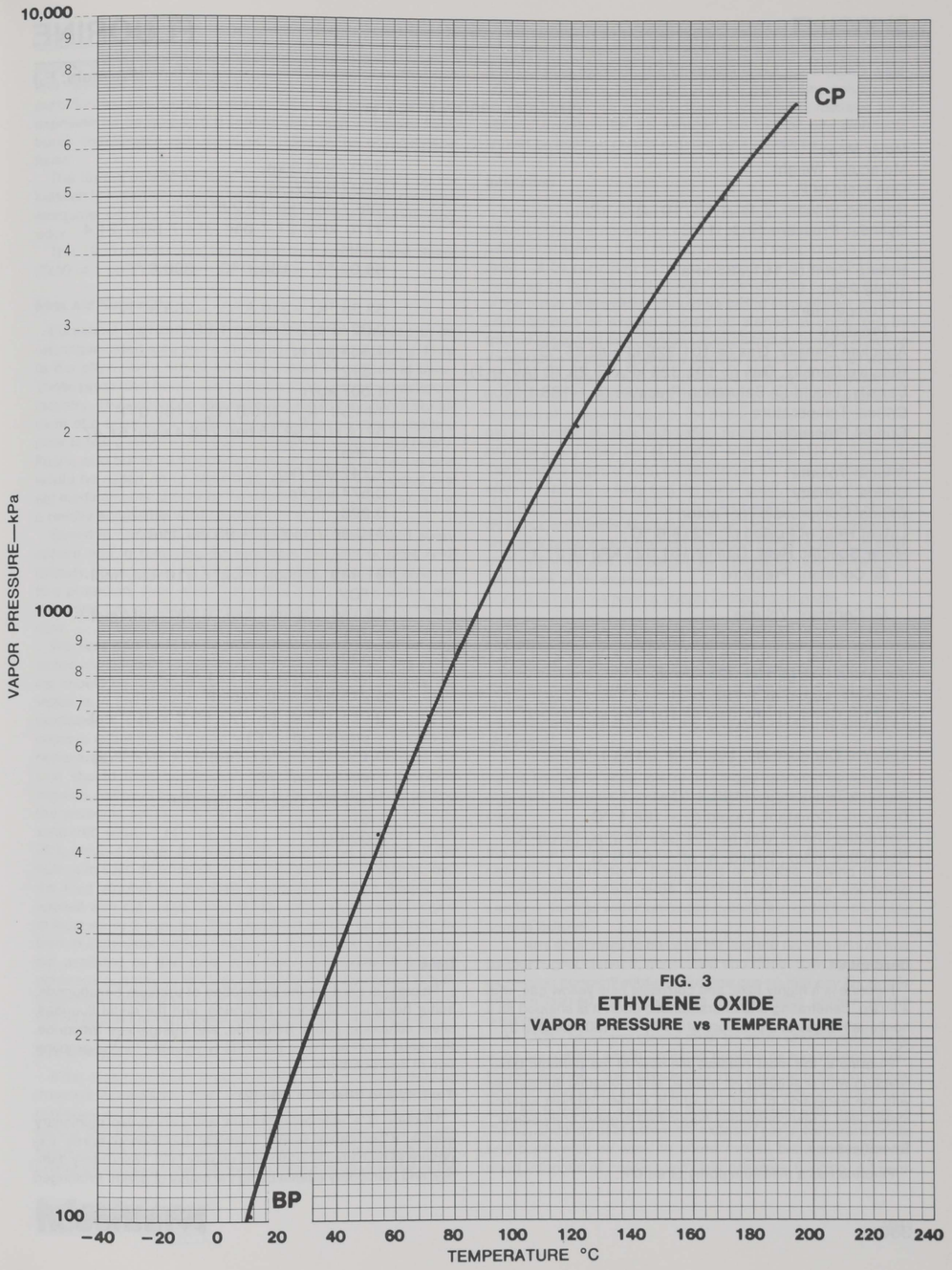


FIG. 3
ETHYLENE OXIDE
VAPOR PRESSURE vs TEMPERATURE

(Formula: F_2)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.037 996 8 kg
One Mole of F_2	0.037 996 8 kg
Specific Volume @ 21.1 °C, 101.325 kPa	636.7 dm^3/kg; 10.2 ft^3/lb
Cylinder Pressure @ 21.1 °C	2170 kPa; 21.7 bar; 314.7 psia; 21.4 atm
Boiling Point @ 101.325 kPa	85.02 °K; −188.1 °C; −306.6 °F
Triple Point	
Temperature	53.34 °K; −219.6 °C; −363.3 °F
Pressure	0.22 kPa; 2.2 mbar; 1.66 mmHg
Absolute Density, Gas @ 101.325 kPa @ 25 °C	1.554 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.312
Density, Liquid @ Saturation Pressure @ −188.1 °C	1.507 kg/l
Critical Temperature	144.30 °K; −128.8 °C; −199.0 °F
Critical Pressure	5215 kPa; 52.15 bar; 756.4 psia; 51.47 atm
Critical Volume	1.742 dm^3/kg
Critical Density	0.574 kg/dm^3
Critical Compressibility Factor	0.288
Latent Heat of Fusion @ −219.6 °C	510.36 J/mol; 121.98 cal/mol
Molar Specific Heat, Gas @ 101.325 kPa @ 21.1 °C	
@ Constant Pressure	31.449 J/(mol· °C); 7.516 cal/(mol· °C)
@ Constant Volume	23.165 J/(mol· °K); 5.537 cal/(mol· °C)
Specific Heat Ratio, Gas @ 101.325 kPa @ 21.1 °C, Cp/Cv	1.358
Viscosity, Gas @ 101.325 kPa @ 0 °C	0.021 80 mPa·s; 0.021 80 cP
Viscosity, Liquid @ −192.2 °C	0.275 mPa·s; 0.275 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 0°C	0.024 763 W/(m· °K); 59.2×10^{-6} cal· cm/(s·cm^2· °C)
Thermal Conductivity, Liquid @ −188.1 °C	0.159 W/(m·°K); 380.0×10^{-6} cal· cm/(s·cm^2·°C)
Surface Tension @ −193.2 °C	14.81 mN·m; 14.81 dyn/cm
Dielectric Constant, Liquid @ −188.1 °C	1.510
Refractive Index, Gas @ 101.325 kPa, n_D @ 25 °C	1.000 187
Refractive Index, Liquid, n_D at −188.1 °C	1.2

Description

Fluorine is a highly toxic and corrosive pale yellow gas, with a sharp, penetrating and characteristic odor. It is shipped as a nonliquefied gas at a pressure of 2 070 kPa (300 psig) at 21.1 °C.

Fluorine is the most reactive member of the periodic table, reacting with practically all organic and inorganic substances with the exception of metal fluorides in their highest valence states, and a few completely fluorinated organic compounds.

Specifications

Fluorine has a minimum purity of 98.0%.

Uses

Fluorine is used for the production of uranium hexafluoride, sulfur hexafluoride, boron trifluoride, and the metal fluorides, silver difluoride, cobalt trifluoride, and manganese trifluoride, the metal fluorides being particularly valuable for the preparation of fluorocarbons.

Toxicity and Effects In Man (2)

Fluorine is a pulmonary irritant and can cause pulmonary edema. It can cause severe chemical and thermal burns. Exposure to high concentrations is usually fatal, respiratory damage and pulmonary edema being the cause of death. Prolonged exposure to as little as 5–10 ppm causes irritation of the eyes and nasal and buccal mucosa. On the skin direct exposure to pure fluorine can cause severe burns in 0.2 second, and an exposure for as long as 0.6 second can result in thermal flash burns comparable with those produced by an oxyacetylene flame.

The lowest published toxic concentration in humans by inhalation is reported to be 25 ppm/5 minutes. Fluorine provides adequate warning of its presence by its sharp, penetrating odor.

The 1979 ACGIH has established a Threshold Limit Value (TLV) of 1 ppm (2 mg/m^3) for fluorine.

First Aid Suggestions

Personnel overcome by fluorine should be removed to an uncontaminated area and a physician called immediately. Prior to the physician's arrival first aid should be started at once. Those presented herein are believed to be common practice in industry. Their adoption should be subject to the prior endorsement of a competent medical advisor. It is recommended that prior to using fluorine, medical treatment of fluorine and hydrofluoric acid burns be discussed with all medical personnel who would be called on to administer aid. The recommended first aid medicaments should be on hand at all times and stored in a readily accessible safe location.

Speed in removing the victim from the contaminated atmosphere and in removing fluorine from the skin or eyes is of primary importance. All affected persons, should be referred to a physician, even when immediate injury seems slight, and the physician should be given a detailed account of the accident.

Workers who have had contact with fluorine should be subjected immediately to a drenching shower of water. The clothing should be removed as rapidly as possible, even while the victim is in the shower, and medical assistance obtained immediately. It is essential that the exposed area be washed with copious quantities of water for a sufficient period of time to remove all fluorine from the skin. The exposed areas of the skin should then be flushed with 2–3% aqueous ammonia solution, followed by liberal rinses of fresh water. Avoid getting the ammonia solution in the eyes. Following this, an ice-cold saturated solution of magnesium sulfate (Epsom salt) or iced 70% alcohol should be applied for at least 30 minutes. If the burn is in such an area where it is impractical to immerse, then the iced alcohol or the iced magnesium sulfate should be applied with saturated compresses, which should be changed at least every 2 minutes. The physician should be available by then to administer further treatment. If, however, a physician is not available by that time, it is then permissible to apply a generous quantity of thick paste made from powdered U.S.P. magnesium oxide and U.S.P. glycerin. Oils and greases should not be applied except under instructions from a physician.

Eye Contact

If the eyes have been in contact with fluorine, they should be irrigated immediately and copiously with clean water for a minimum of 15 minutes. The eyelids should be held apart during the irrigation to insure contact of water with all the tissues of the surface of the eyes and lids. A physician, preferably an eye specialist, should be called in attendance at the first possible moment. If a physician is not immediately available, instill one or two drops of 0.5% pontocaine solution, or an equally effective aqueous topical anesthetic, followed by a second irrigation for 15 minutes. No oils or oily ointments should be instilled unless ordered by a physician.

Inhalation

A worker who is suspected of a possible severe exposure to gaseous fluorine should be carried at once into an uncontaminated atmosphere. Even in the absence of symptoms, a worker must not be permitted to return to work for at least 24 hours because of the potential danger of developing severe edema of the lungs. A physician should be called immediately and the administration of oxygen should be started at once, but by trained personnel only. Oxygen administration is most effective if expiration is made against a positive pressure 4 cm of water. Oxygen inhalation must be continued as long as necessary to maintain the normal color of the skin and mucous membranes. In cases of severe exposure, the patient should breathe 100% oxygen under positive exhalation pressure for one-half hour periods every hour for at least 3 and preferably 6 hours. If there are no signs of lung congestion at the end of this period, and if breathing is easy and the color good, oxygen inhalation may be discontinued. Throughout this period the patient should be kept comfortably warm but not hot. Under no circumstances should a patient be permitted to return home or back to work until examined and discharged by a physician who is aware of the nature of his exposure.

Always have on hand a supply of magnesia paste.

Precautions in Handling and Storage

Although fluorine is the most reactive element and recognized as a very dangerous material, it can be handled without undue hazards if proper precautions are taken. In order to minimize the risks involved, the following measures should be observed.

1. In handling fluorine under pressure, remote-controlled valves should be used, preferably those operated by manually actuated extension handles passing through a suitable barricade.

2. Regulators or double valving should be employed near the source of high pressure fluorine in order to facilitate a safe reduction of pressure. Regulators or double valving is also recommended where large quantities of fluorine are being handled, such as with manifolded cylinders in order to minimize control failures.

3. Any equipment to be used for fluorine service should first be thoroughly cleaned, degreased and dried, then treated with increasing concentrations of fluorine gas so that any impurities may be burned out without the simultaneous ignition of the equipment.

4. Clean neoprene gloves must be worn when directly handling equipment which contains fluorine or has recently contained fluorine. This precaution not only affords protection against fluorine but also against films of hydrofluoric acid which may be formed by escaping fluorine reacting with moisture in the air, and may coat externally exposed parts. Neoprene coats and boots may be worn to afford overall body protection for short intervals of contact with low pressure fluorine. All such

protective clothing should be designed and used, however, in such a manner that it can be shed easily and quickly.

5. Safety glasses should be worn at all times. Metal frames rather than the customary plastic are desirable to eliminate the possibility of the frames catching fire.

6. Avoid repeated bending or excessive vibration of piping or equipment. Such mechanical actions can result in a flaking of the protective fluorine film, resulting in a rupture of the metal with or without the occurrence of a fluorine-metal flame. Flaking, furthermore, can be accompanied by dusting with the resultant fouling of valves.

7. Any equipment that has contained fluorine must be thoroughly purged with a dry inert gas (such as nitrogen) and evacuated prior to opening or refilling. If the quantity of fluorine to be purged is large, the purge system should include a fluorine-hydrocarbon-air burner, scrubber and stack to prevent any undue exit hazards. A soda lime tower followed by a drier should be included in the vacuum line to pick up trace amounts of fluorine in order to protect the vacuum pump.

8. Face shields made of conventional materials, or preferably chemically-resistant polymers, should be worn whenever operators must approach equipment containing fluorine under pressure. All face shields afford limited, though valuable, protection against air blasts of fluorine.

9. All areas containing fluorine under pressure should be inspected for leaks at suitable intervals. All leaks should be repaired at once but not while the system contains fluorine. Ammonia vapor expelled from a squeeze bottle (containing ammonium hydroxide) at suspected points may be used to detect leaks. Filter paper moistened with potassium iodide solution is a very sensitive means of detecting fluorine (down to about 25 ppm). The potassium iodide paper should be held with the aid of 18–24" long metal tongs or forceps. The odor of fluorine is sufficiently strong so that it can be detected in very low concentrations. Fluorine will also fume readily in air.

10. Adequate ventilation is essential. There should be a minimum of 10 air changes per hour for enclosed spaces. Portable floor level 36" fans are desirable for auxillary ventilation at outdoor installations or semi-open installations.

11. Positive instant-acting types of safety showers and eye-washing fountains should be strategically located near the area where fluorine is being used. These should be tested at least weekly.

12. Air-line hose masks should be located in strategic positions for use in emergencies.

13. All equipment, pipe lines, etc., should be identified by distinctive colors and signs.

14. It is recommended that personnel work in pairs and within sight and sound of each other, but not in the same immediate working area. Only trained and competent personnel should be permitted to handle fluorine. Frequent checks should be made of the operation.

15. An alarm system should be provided in order that the area may be alerted and cleared if needed.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

All lines and equipment to contain fluorine should be pretested for leaks with dry nitrogen.

In addition, detection devices are available for continuously monitoring small concentrations of fluorine in air.

Disposal of Leaking Cylinders

Cylinders containing fluorine which develop leaks that cannot be corrected may be treated in the following manner.

Absorb the fluorine in a large volume of water. Hydrofluoric acid, oxygen, and traces of hydrogen peroxide and oxygen difluoride are formed. The solution can then be transferred to the plant disposal unit for neutralization and disposal.

Materials of Construction

The reaction of fluorine with many metals is slow at room temperature and often results in the formation of a metal fluoride film (see Passivation Procedure). This film retards further attack in the case of certain metals such as brass, iron, aluminum, magnesium and copper and hence these metals are quite satisfactory for handling fluorine at room temperatures. Nickel and monel are by far the best materials to use at high temperatures.

Recommended Controls

Gaseous fluorine has been handled successfully in contact with a variety of materials of construction. Matheson makes available the following items which have been tested and recommended for normal handling of fluorine. All fluorine equipment, except the flowmeters and Hydrogen Fluoride Trap, have been passivated with fluorine.

Valves

Metering valve Model 940F with ¼" compression inlet and outlet connections is recommended. This valve has an aluminum-silicon-bronze body, stainless needle stem, and Teflon packing.

Gauges

Gauges with monel or stainless steel Bourdon tubes passivated for fluorine service should be used.

Hydrogen Fluoride Trap (Model No. 68-1008)

Commercial fluorine may contain up to 0.2% hydrogen fluoride and it may be desirable to reduce the hydrogen fluoride concentration to a negligible amount for certain operations (particularly when fluorine is to be used with laboratory glassware). Removal of the hydrogen fluoride can be accomplished by passing the fluorine through a sodium fluoride trap.

A convenient laboratory scale trap complete with sodium fluoride, heating coil, ¼" flare connections, and thermometer well, is available from Matheson.

Prior to use, the trap must be activated by plugging the heating coil into a Variac which can be adjusted to heat the system to 250 to 300 °C while purging with dry nitrogen. Completion of the activation cycle can be determined by holding filter paper soaked in potassium iodide solution in the exit stream. The paper will brown until the unit is completely reactivated. The absorber, when cooled to room temperature, is ready for hydrogen fluoride absorption. The trap is suitable for processing 18 to 24 lb of fluorine gas before reactivation is necessary.

Flowmeters (Model 7825)

Flowmeters with stainless steel end fitting constructions, Pyrex tubes and Teflon packing are available from Matheson.

It is recommended that these meters be frequently calibrated with dry nitrogen or argon in order to compensate for errors introduced by the inevitable slow etching of the glass tube. The use of argon for calibration purposes is advantageous because its density is similar to fluorine.

Barricade and Remote Control Systems (Model No. 68-1009)

Barricades are necessary to protect the operator from any metal ignition which conceivably could occur in any part of a system containing fluorine under high pressure.

Complete barricades with remote valve controls are available from Matheson to accomodate different size fluorine cylinders. These barricades can be fabricated to fit General Chemical fluorine cylinders.

Pressure Regulating System

A pressure reducing regulator designated as Model B15F-679 has been developed by Matheson specifically for fluorine. The regulator is degreased and passivated and is ready for immediate use in fluorine service. The regulator can be adapted for use with a barricade.

The automatic pressure regulator is used to reduce cylinder pressure to a safe value, consistent with system's design. The control pressure may be varied from 28-340 kPa (4-50 psig). The control pressure will remain essentially constant, despite a drop in cylinder pressure. In cases where the flow is impeded or stopped, the regulator will "lock up," preventing build-up of dangerous pressures.

Manual Valves

Manual needle value Model 55F-679 is available for direct connection to the cylinder valve outlet. It is equipped with a ¼" compression fitting on outlet. It should be used only for intermittent flow control and not as a pressure control.

Another method of flow control is a system of double valving. This system lacks the convenience of the regulator; however, it has proven satisfactory for laboratory set-ups.

Double valving should be employed near the source of high pressure fluorine in order to facilitate a safe reduction of flow.

A double valving arrangement complete with inlet connection to fit the fluorine cylinder valve, Model No. 68-1011 is available from Matheson. This double valving arrangement is constructed to adapt to the barricade system.

Blow-Out Traps

The use of simple blow-out traps of the test tube type commonly used in laboratories to warn of the blocking of lines or vessels is recommended. They are filled with chlorotrifluoroethylene (Kel-F) polymer oil. The head of oil should not exceed a nominal six inches.

Lines and Fittings

All threaded connections should be back brazed, silver soldered or welded. Flare or compression fittings may be utilized whenever "make or break" joints are required. If threaded connections must be used, an aqueous Teflon dispersion pipe dope should be applied to the threads after the first two threads are engaged.

Passivation Procedure

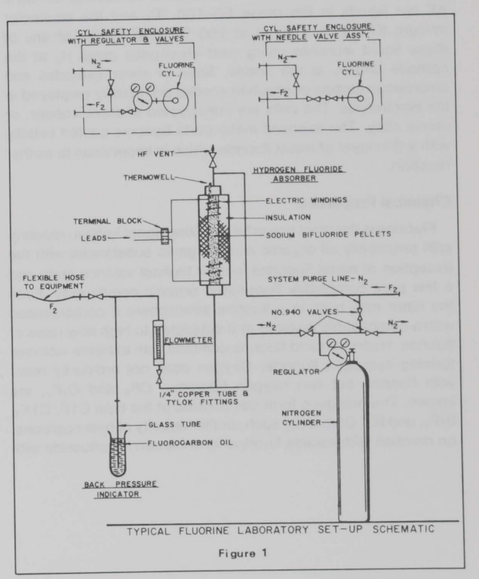
Prior to the placing of any equipment, lines or fittings in service, they must be thoroughly cleaned of all foreign matter, flushed with a nonaqueous degreasing solvent such as acetone, trichloroethylene or carbon tetrachloride, then thoroughly purged with a stream of dry nitrogen. The equipment is then ready for passivating.

The passivating procedure consists of slowly displacing the dry nitrogen in the system by bleeding fluorine into the system (at essentially atmospheric pressure, and a nominal rate of 0.1 to 0.3 mole of fluorine per hour for laboratory sized systems). Continue the displacement procedure until a piece of filter paper or swatch of cotton held close to the exit by means of long metal forceps, begins to burn. The system is then valved off and the working pressure of fluorine is applied. After five to ten minutes, passivation is assumed to be complete. The fluorine system is then flushed with dry nitrogen and sealed until put into service.

Passivation may also be achieved by use of chlorine trifluoride in the manner described for fluorine.

Typical Laboratory Set-Up

Refer to Figure 1.



TYPICAL FLUORINE LABORATORY SET-UP SCHEMATIC

Figure 1

Cylinder and Valve Description

Fluorine is packaged in and shipped in DOT approved high pressure cylinders with a minimum service pressure of 6 895 kPa (1 000 psig) for standard steel cylinders and 2 758 kPa (400 psig) for nickel cylinders. The cylinder is equipped with Compressed Gas Association (CGA) standard valve outlet connection No. 679. The valve outlet has a thread size of 1.030 inches diameter (see Figure 2).

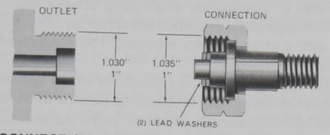


Fig. 2. CONNECTION 679 1.030″-14 LH EXT. using Small Flat Seat with Washer

Safety Devices

No safety devices are used on cylinders of fluorine.

Shipping Regulations

Fluorine is classified by the DOT as a flammable, compressed gas and is shipped under a DOT "Red Gas Label."

Commercial Preparations

Elemental fluorine is prepared by electrolyzing a mixture of KF dissolved in anhydrous HF. Mixtures containing less than 30% KF are liquid below 0 °C, mixtures containing 40–65% KF are liquids in the range 50–100 °C, and the equimolar mixture KF·HF is a liquid at 250 °C. Electrolysis of any of these liquid mixtures using inert electrodes gives H_2 at the cathode and F_2 at the anode. Steel or silver cathodes and amorphous carbon or graphite anodes are usually employed in the electrolysis. The cells are constructed of steel, copper, or monel alloy. The exposed metal parts become coated initially with a thin layer of metal fluoride which is impervious to further reaction.

Chemical Properties

Fluorine is the most powerful oxidizing agent known, reacting with practically all organic and inorganic substances with the exception of metal fluorides in their highest valence state and a few pure completely fluorinated organic compounds. Even the latter may burn in a fluorine atmosphere if contaminated with a combustible material or if subjected to high flow rates of fluorine. Hydrogen and fluorine combine with extreme violence forming hydrogen fluoride. Oxygen does not ordinarily react with fluorine but two oxygen fluorides, OF_2 and O_2F_2, are known. The halogens form compounds of the type ClF, ClF_3, BrF_3, and IF_5. Carbon as such, or the majority of hydrocarbons, on reaction with excess fluorine form carbon tetrafluoride with small amounts of tetrafluorethylene or hexafluoropropene. Nitrogen is generally inert toward fluorine and may be used as a diluent for vapor-phase reactions. Fluorine will displace other halogens from many such halogen-containing compounds. The reaction of most organic compounds with fluorine will occur explosively.

For a complete review of the chemical properties of fluorine, see Reference 3.

Thermodynamic and Detailed Physical Data

Molecular Structure

The homopolar fluorine molecule, with $D_{\infty h}$ symmetry and a symmetry number of two, is not infrared active, but is Raman active. The fundamental vibrational frequency is 923.1 cm^{-1}, and the F—F bond distance is 1.409 Å (1.409 × 10^{-10} m) (1).

Vapor Pressure (4)

The vapor pressure of liquid fluorine is shown below.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
53.56	0.223	2.2	1.67
59.03	1.179	11.8	8.84
65.02	4.704	47.0	35.28
71.07	14.561	145.6	109.22
77.17	37.383	373.8	280.40
83.06	80.542	805.4	604.12
85.05	101.735	1 017.4	763.08
86.60	120.932	1 209.3	907.07
88.59	149.626	1 496.3	1 122.29
89.40	162.638	1 626.4	1 219.89

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/kg
80	177.515
85.03	166.356
95	155.145

Thermodynamic Properties of Fluorine As Ideal Gas @ 25 °C (5)

Heat Capacity, $C°_p$	31.338 J/(mol·°K)
Entropy, S^0	202.702 J/(mol·°K)
Free Energy Function $(F^0_{298} - H^0_{298})/298$	−202.702 J/(mol·°K)
Enthalpy Difference, $H^0_{298} - H^0_O$	8.828 kJ/mol
Enthalpy of Formation, H^0_f	0.000 kJ/mol
Free Energy of Formation, F^0_f	0.000 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of fluorine, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] M. B. Jacobs, The Analytical *Toxicology of Industrial Inorganic Poisons*, *1967*, p. 659, John Wiley & Sons, Inc., New York, New York.

[3] H. R. Neumark and J. M. Siegmund, in Kirk-Othmer's *Encyclopedia of Chemical Technology*, 2nd edition, *1966*, Volume 9, pp. 507–509, John Wiley & Sons, Inc., New York, New York.

[4] J. H. Hu, D. White, and H. L. Johnston, *J. Amer. Chem. Soc.* 75, 5642–5645 (1953).

[5] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

FLUOROFORM

(Synonyms: Freon-23®; Trifluoromethane)
(Formula: CHF_3)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.070 014 kg
One Mole of CHF_3	0.070 014 kg
Specific Volume @ 21.1 °C, @ 101.325 kPa	343.3 dm^3/kg; 5.5 ft^3/lb
Vapor Pressure @ 21.1 °C	4 480 kPa; 44.8 bar; 649.7 psia; 44.2 atm
Boiling Point @ 101.325 kPa	191.12 °K; −82.0 °C; −115.6 °F
Freezing Point	117.95 °K; −155.2 °C; −247.4 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	2.86 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	2.417
Density, Liquid @ Saturation Pressure @ −80 °C	1.440 kg/l
Critical Temperature	298.89 °K; 25.7 °C; 78.3 °F
Critical Pressure	4 810 kPa; 48.1 bar; 697.0 psia; 47.43 atm
Critical Volume	1.904 dm^3/kg
Critical Density	0.525 kg/dm^3
Critical Compressibility Factor	0.259 4
Latent Heat of Fusion @ −155.2 °C	57.96 kJ/kg; 13.85 kcal/kg
Dipole Moment	5.4×10^{-30} C·m; 1.62 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	51.557 J/(mol· °K); 12.322 cal/(mol· °C)
Molar Specific Heat, Liquid @ −100 °C	84.805 J/(mol· °K); 20.269 cal/(mol· °C)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.014 4 mPa·s; 0.014 4 cP
Viscosity, Liquid @ −80 °C	0.368 mPa·s; 0.368 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	$0.015\ 06$ W/(m· °K); 36.0×10^{-6} cal· cm/(s·cm^2· °C)
Thermal Conductivity, Liquid @ −80 °C	$0.175\ 7$ W/(m· °K); 419.9×10^{-6} cal· cm/(s·cm^2· °C)
Solubility In Water @ 101.325 kPa @ 25 °C	0.10% (by weight)
Refractive Index, Liquid, n_D @ −73.3 °C	1.215
Relative Dielectric Strength (Nitrogen = 1)	1.04

Description

Fluoroform is a colorless, nonflammable, nontoxic gas at temperatures above 298.89 °K (25.75 °C) at atomospheric pressure. It is shipped in steel cylinders as a liquefied gas under its own vapor pressure of 4 380 kPa (635 psig) at 21.1 °C.

Specifications

Fluoroform has a minimum purity of 98.0%.

Uses

Fluoroform is of interest as a refrigerant and as an intermediate in organic synthesis.

Toxicity And Effects In Man (2)

Inhalation of high concentrations of gas can cause such symptoms as dizziness, disorientation, incoordination, narcosis, nausea or vomiting. There appear to be no irreversible effects once the oxygen deficiency has been corrected.

Contact of liquid fluoroform with the skin can cause frostbite.

First Aid Treatment (2)

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is

overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration and oxygen simultaneously. Treat symptomatically thereafter.

Skin Contact

In case of skin contact with liquid fluoroform, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Leak Detection

Leaks of fluoroform may be detected by painting the suspected points with soap water solution. Leaks will be evident by the formation of bubbles. In addition, the Matheson Leak detector Models 8016 and 8017 provide a more sensitive measure of leak detection.

Disposal of Leaking Cylinders

Cylinders containing fluoroform which develop leaks that cannot be corrected normally may be disposed of by the procedure described in Appendix II-C.

Materials of Construction

Since fluoroform is noncorrosive any common construction metal may be used with fluoroform under normal conditions of use. At high temperatures some metals may act as catalysts in the decomposition of fluoroform.

Cylinder and Valve Description

Fluoroform is shipped in DOT approved steel cylinders. Cylinders containing fluoroform are equipped with brass valves with the alternate standard Compressed Gas Association (CGA) outlet connection No. 320. The valve outlet has a thread size of 0.825 inch, with right-hand external threads, with a flat seat and washer (see Figure 1). Lecture bottles have a special 5/16

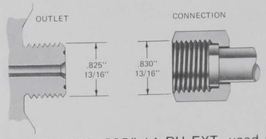


Fig. 1. CONNECTION 320 .825"-14 RH EXT. used with Flat Seat and Washer

inch-32 threads per inch, female outlet and a 9/16 inch-18 threads per inch male dual valve outlet.

Safety Devices

Cylinders containing fluoroform have frangible discs as safety devices. Cylinders should, therefore, be stored away from sources of heat to avoid developing pressures capable of rupturing the disc.

Recommended Controls

Automatic Regulators

The following types of automatic pressure regulators are available for use with fluoroform:

1. Single Stage Regulators

The single stage regulator will reduce cylinder pressure in one stage to a delivery pressure in a particular range depending on the design of the regulator and its spring load. These regulators will show a slight variation in delivery pressure as cylinder pressure. The following single stage regulators are available for use with fluoroform:

Model No.	Delivery Pressure Range kPa	bar (g)	psig
1P-320	28–240	0.28–2.4	4–35
1L-320	28–550	0.28–5.5	4–80
1H-320	69–1 240	0.69–12.4	10–180
2-320	340–4 480	3.4 –44.8	50–650
3320 (for lecture bottles only)	28–410	0.28–4.1	4–60
3321 (for lecture bottles only)	28–410	0.28–4.1	4–60

2. Two Stage Regulators

These regulators perform the same function as single stage regulators. However, greater accuracy in control of delivery pressure is maintained since the delivery pressure does not vary as cylinder pressure falls. The following two stage regulators are available for use with fluoroform:

Model No.	Delivery Pressure Range kPa	bar (g)	psig
8L-320	14–104	0.14–1.04	2–15
8-320	28–340	0.28–3.4	4–50
8H-320	69–690	0.69–6.9	10–100
9-320	138–1720	1.38–17.2	20–250

To prevent suckback of foreign materials, a check valve is recommended for use with the above regulators.

Manual Controls

Matheson needle valve Model 50-320, a brass bar stock valve, is recommended for direct connection to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, 1/4" compression fitting, or 1/4" NPT male or female pipe. It should be used only where manual flow is needed, but this requires close supervision. It should not be used as a pressure control since it will not prevent excessive pressure from developing if the system becomes clogged or is closed. A Model 31B manual needle valve is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Fluoroform is classified by the DOT as a nonflammable compressed gas and is shipped with the required "Green Label."

Commercial Preparation

Fluoroform has been prepared by the liquid phase exchange reaction of chloroform with antimony fluoride-hydrogen fluoride at temperatures above 125 °C and at high pressures. $CHClF_2$ and $CHCl_2F$ in the presence of aluminum chloride at 0 °C disproportionate to form chloroform and fluoroform. An electrochemical process promises to make fluoroform a commercial chemical; starting materials such as acetic acid, acetone, and trimethylamine yield substantial proportions of fluoroform.

Chemical Properties

Since it is almost inert, the reactions of fluoroform are principally those of decomposition. It reacts with N_2O_3 above 175 °C and with NOF at about 100 °C. Lime at a dull red heat destroys fluoroform, and similar temperatures are required for rapid reaction with most metals. Photochemical chlorination is very slow and photobromination has been unsuccessful. The thermal halogenation reactions proceed in excellent yields without difficulty.

Thermodynamic and Detailed Physical Data

Molecular Structure

Fluoroform has C_{3v} symmetry and a symmetry number of three, with C—F and C—H bond distances of 1.333 Å (1.333 × 10^{-10} m) and 1.098 Å (1.098 × 10^{-10} m), respectively, and F—C—F and F—C—H bond angles of 108.6 ± 0.5 ° and 110.33 °, respectively (1).

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous fluoroform.

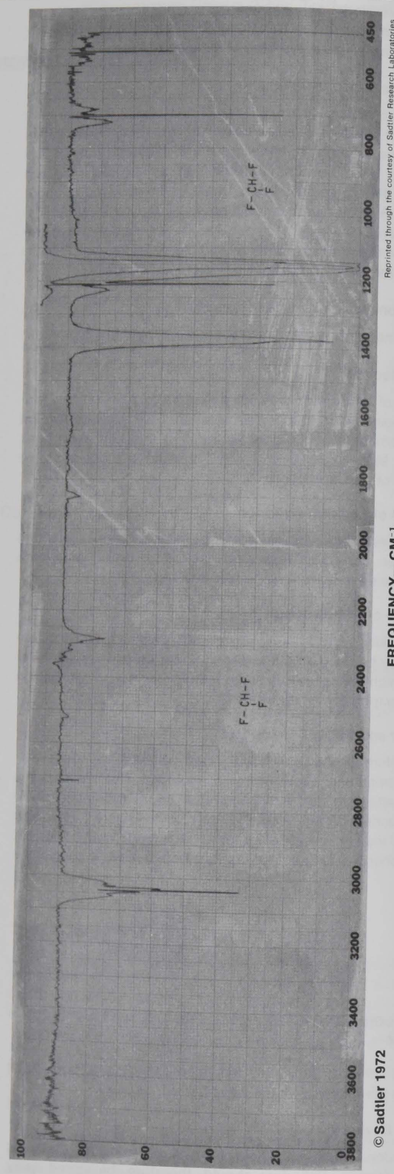


Fig. 2. Infrared spectrum of gaseous fluoroform over the frequency region of 3 800 cm^{-1} to 450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure: curve A (complete scan): 2.667 kPa (20 mmHg), curve B (partial scan): 0.067 kPa (0.5 mmHg) (6).

Vapor Pressure

Vapor pressure data from 145.348 °K to 191.177 °K are shown below (3).

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
145.348	2.720	27.2	20.4
158.080	9.466	94.7	71.0
164.201	16.451	164.5	123.4
169.182	23.838	238.4	178.8
172.824	31.264	312.6	234.5
176.426	40.329	403.3	302.5
179.349	49.169	491.7	368.8
182.000	58.568	585.7	439.3
183.882	66.007	660.1	495.1
185.917	74.820	748.2	561.2
187.889	84.446	844.4	633.4
189.551	93.219	932.2	699.2
191.177	102.512	1 025.1	768.9

Vapor pressure data from 191.12 °K (boiling point) to 298.89 °K (critical point) are shown below (4).

Temperature, °K	Vapor Pressure kPa	bar	atm
191.12	101.325	1.013	1.000
203.15	193.733	1.94	1.912
213.15	313.702	3.14	3.096
223.15	482.631	4.83	4.763
233.15	706.701	7.07	6.975
243.15	979.040	9.79	9.662
253.15	1 399.62	14.0	13.81
263.15	1 896.04	19.0	18.71
273.15	2 413.16	24.1	23.82
283.15	3 261.65	32.6	32.19
293.15	4 171.55	41.7	41.17
298.89	4 805.85	48.1	47.43

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv

Temperature, °C	ΔHv, kJ/kg
−120	263.80
−100	251.24
−82.0	238.67

Thermodynamic Properties of Fluoroform As Ideal Gas @ 25 °C (5)

Heat Capacity, $C°_p$	51.041 J/(mol·°K)
Entropy, $S°$	259.542 J/(mol·°K)
Free Energy Function, $(F°_{298} - H°_{298})/298$	−259.542 J/(mol·°K)
Enthalpy Difference, $H°_{298} - H°_0$	11.564 kJ/mol
Enthalpy of Formation, $\Delta H°_f$	−697.054 kJ/mol
Free Energy of Formation, $\Delta F°_f$	−662.624 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of fluoroform, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 119–123, Matheson, Lyndhurst, New Jersey.

[3] R. H. Valentine, G. E. Brodale, and W. F. Giauque, *J. Phys. Chem.* 66, 392 (1962).

[4] *Freon Fluorocarbons*, Tech. Bull. B-2, *1964*, E. I. duPont de Nemours & Co., Inc., Wilmington, Delaware.

[5] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[6] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

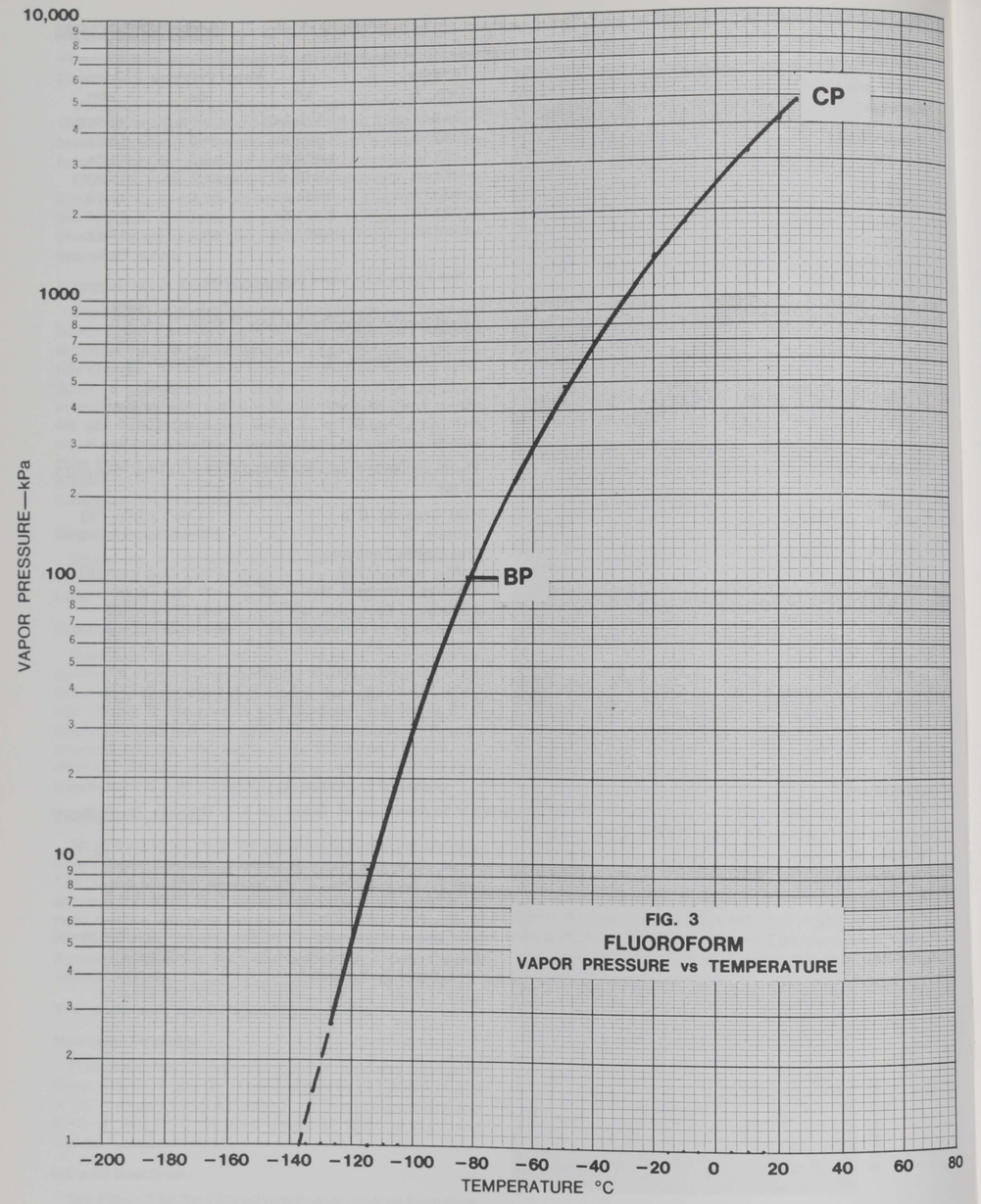


FIG. 3
FLUOROFORM
VAPOR PRESSURE vs TEMPERATURE

Matheson

GERMANE

(Synonyms: Monogermane; Germanium Tetrahydride; Germanomethane)
(Formula: GeH_4)

PHYSICAL PROPERTIES (1)

Molar Mass	0.076 662 kg
Molecular Weight	0.076 662 kg
One Mole of GeH_4	315.3 dm^3/kg; 5.05 ft^3/lb
Specific Volume @ 21.1 °C, 101.325 kPa	184.80 °K; −88.4 °C; −127.0 °F
Boiling Point @ 101.325 kPa	107.25 °K; −165.9 °C; −266.6 °F
Melting Point	3.420 kg/m^3
Absolute Density, Gas @ 101.325 kPa @ 0 °C	2.645
Relative Density, Gas @ 101.325 kPa @ 0 °C (Air = 1)	1.523 kg/dm^3
Density, Liquid @ −142.0 °C	308.0 °K; 34.8 °C; 94.7 °F
Critical Temperature	5 553 kPa; 55.53 bar; 805.3 psia; 54.8 atm
Critical Pressure	1.671 dm^3/kg
Critical Volume	0.598 kg/dm^3
Critical Density	0.276
Critical Compressibility Factor	835.54 J/mol; 199.7 cal/mol
Latent Heat of Fusion @ −165.9 °C	1.000 894
Refractive Index, Gas @ 101.325 kPa. n_D @ 0 °C	15.80 mN/m; 15.80 dyn/cm
Surface Tension @ −88.4 °C	

Description

Germane is a toxic, flammable, colorless gas, with a characteristic pungent odor at room temperature and atmospheric pressure. It is shipped in 0.1 kg quantities at a pressure of 360 kPa (52 psig) at 21.1 °C.

Specifications

Matheson supplies a Semiconductor Grade of germane. This grade has a minimum purity of 99.9%.

Uses

Germane is used chiefly for the production of high purity germanium, which is used in semiconductors such as transistors.

Toxicity and Effects In Man (2)

Like arsine, germane has been shown to be a hemolytic agent. The symptoms produced may be similar to those produced by arsine, i.e., malaise, difficulty in breathing, severe headache, giddiness, fainting fits, nausea, vomiting and gastric disturbances. Because of properties which are similar to those of arsine, it might be anticipated to cause hemolysis and renal damage after significant exposure. The 1979 ACGIH has recommended a Threshold Limit Valve (TLV) of 0.2 ppm (0.6 mg/m^3) for germane.

First Aid Treatment

Treatment of germane poisoning is unknown at this time; however, several guidelines can be proposed, which are based on successful treatment of arsine gas poisoning. Usual medical supportive measures, such as, oxygen administration, pressor agents, cardiac monitoring, and intensive care unit admission, should be undertaken as soon as possible. Mannitol induced diuresis should be instituted early. Ready availability of a renal hemodialysis unit is strongly recommended. Peritoneal dialysis has been reported to be effective in cases of arsine poisoning. In cases of extreme hemolysis, exchange transfusions have proved exceptionally helpful, particularly in cases of severe arsine poisoning and this measure should be considered when faced with this problem.

Precautions in Handling and Storage

Germane is hazardous because of its high toxicity and flammability. Germane should be used in a well-ventilated area, preferably in a hood with forced ventilation. Personnel handling and using germane should have available, for immediate use, oxygen generating gas masks of a type approved by NIOSH, or approved self-contained breathing apparatus. Additional gas masks should be located in convenient areas near where the germane is being used, in case of emergency. Do not store reserve stocks of germane with cylinders containing oxygen or other highly oxidizing or flammable materials. Ground all lines and equipment used with germane.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Piping and equipment should be thoroughly pressure-checked with an inert gas, such as nitrogen, above working pressures and be completely leak-tight.

Matheson

Materials of Construction

Piping and accessories leading to equipment for the thermal decomposition of germane may be of iron or steel construction and should be adequately designed to withstand pressures to be encountered.

Cylinder and Valve Description

Germane is supplied in DOT approved steel cylinders. Only 1 size cylinder, 3P, containing 0.1 kg is available. The cylinders are equipped with valves having Compressed Gas Association No. (CGA) alternate standard 660 valve outlets. The valve outlet has a thread size of 1.030″, with right-hand external threads with a flat seat and using a washer as a seal (see Figure 1 for an illustration of this valve outlet and its mating connection).

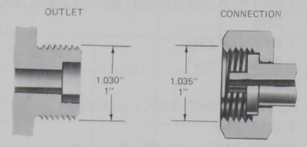


Fig. 1. CONNECTION 660 1.030″-14 RH EXT. using Flat Seat with Washer

Germane mixtures are shipped in DOT approved steel cylinders which are equipped with valves having Compressed Gas Association (CGA) No. 350 valve outlets. The valve outlet has a thread size of 0.825″, with left-hand external threads accepting a round-shaped nipple.

Safety Devices

Cylinders containing germane are not equipped with safety devices, and therefore should be stored away from sources of heat to avoid the development of dangerous pressures within the cylinder.

Recommended Controls

Automatic Pressure Regulators

Matheson Model 3501-660 is recommended for use with germane. All parts of the regulator, including the diaphragm, in the gas stream are of type 316 stainless steel. It is provided with a Tefzel seat, a packless outlet valve with stainless steel diaphragm, stainless steel delivery pressure and cylinder pressure gauges, and Teflon gaskets. There are no rubber parts. It has a delivery pressure range of 0–170 kPa (0–25 psig).

Single stage regulators Models 3503-350 and 19SM-350, each with delivery pressure ranges of 0–170 kPa (0–25 psig), and the two stage regulators Models 3803-350 and 3104-350, with delivery pressure ranges of 0–100 kPa (0–15 psig) and 28–690 kPa (4–100 psig), respectively, are recommended for use with germane mixtures.

Manual Controls

A Matheson Model 4350-350 brass needle valve is available for direct attachment to the cylinder valve outlet of germane mixtures. Needle valves are equipped with a 12″ length of ¼″ o.d. copper tubing to provide for leak-free connection to the apparatus.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float, of the rotameter type, are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required.Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ±1.2%.

Shipping Regulations

Germane is classified by the DOT as a "Class A" poison and a flammable gas and is shipped under the required "Poison Gas Label" and "Red Gas Label".

Chemical Preparation

The action of acids (hydrochloric acid or sulfuric acid in water), ammonium chloride or bromide in liquid ammonia, or hydrazine hydrochloride in hydrazine on germanium-magnesium alloys and calcium germanides gives a mixture of various germanes (mostly monogermane), the individual compounds being separated by fractional distillation. Monogermane can also be prepared by the reaction of germanium tetra-chloride or tetra-alkoxides with metal hydrides (e.g., LiH) or double hydrides (e.g., $NaBH_4$, $LiAlH_4$, LiAl(Bu-tert)H) in anhydrous organic solvents (ethyl ether, tetrahydrofuran, dioxane). Monogermane can also be obtained in aqueous solution along with small amounts of di- and trigermanes by the reaction of a solution of germanium dioxide in hydrobromic acid, acetic acid, or sulfuric acid with sodium or potassium hydride.

Chemical Properties

Germane is similar to silane in its chemical properties, but generally less reactive. It is not spontaneously flammable as silane. If ignited, it burns to give GeO_2 and H_2O. It is more stable to hydrolysis than silane, being stable to about 30% alkali. At elevated temperatures, germane is decomposed into its elements, germanium deposits of the P type being obtained.

Germane is less stable thermally than silane, decomposing measurably at about 280 °C into germanium and hydrogen, this temperature being over 100 °C below the temperature at which silane decomposes appreciably. Kinetic studies of the decomposition of germane have been made, the initiating step proposed for the homogeneous decomposition being $GeH_4 \rightarrow GeH_2 + H_2$, but the subsequent decomposition of GeH_2 is not clear. Germane reacts with excess oxygen according to the equation:

$$GeH_4 + 2O_2 \rightarrow GeO_2 + 2H_2O$$

Germane reacts with sodium or potassium in liquid ammonia giving the room-temperature unstable solids $NaGeH_3$ and $KGeH_3$, respectively.

For extensive presentation of the chemical properties of the germanium hydrides, see Reference 3.

Thermodynamic and Detailed Physical Data

Molecular Structure

Germane is a tetrahedral molecule with T_d symmetry, with a Ge—H bond distance of 1.54 Å (1.54×10^{-10} m) and a H—Ge—H bond angle of 109.5°.

Infrared Spectrum (1)

Germane has four normal modes of vibration (ν_1–ν_4). The vibrational frequencies (in cm^{-1}) for the four modes are as follows: 2 106 (ν_1); 931 (ν_2); 2 114 (ν_3); 819 (ν_4). All four vibrations are Raman active, whereas only ν_3 and ν_4 are infrared active.

Vapor Pressure (4)

Vapor pressure data up to 101.325 kPa (1 atm) are shown below:

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
110.15	0.133	1.33	1
122.15	0.667	6.67	5
127.85	1.332	13.3	10
133.95	2.665	26.7	20
141.55	5.330	53.3	40
146.45	7.995	80.0	60
152.85	13.331	133.3	100
161.95	26.664	266.6	200
172.95	53.328	533.3	400
184.25	101.325	1 013.25	760

Latent Heat of Vaporization, ΔHv @ −88.4 °C 14.06 kJ/mol; 3.36 kcal/mol

Thermodynamic Properties of Germane As Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	45.020 J/(mol·°K); 10.76 cal/(mol·°C)
Entropy, S°	217.024 J/(mol·°K); 51.87 cal/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	10.700 kJ/mol; 2.567 kcal/mol
Enthalpy of Formation, ΔH_f°	90.793 kJ/mol; 21.7 kcal/mol
Gibbs Energy of Formation, ΔG_f°	113.386 kJ/mol; 27.1 kcal/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of germane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 60–75, Matheson, Lyndhurst, New Jersey.

[3] E. Wiberg, and E. Amberger, *Hydrides of the Elements of Main Groups I–IV*, *1971*, pp. 639–718, Elsevier Publishing Company, Inc., New York, New York.

[4] *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p. 3047, McGraw-Hill Book Co., Inc., New York, New York.

[5] D. D. Wagman, **et al.**, *Selected Values of Chemical Thermodynamic Properties*, *1968*, Natl. Bur. Stand. Tech. Note 270-3, U. S. Government Printing Office, Washington, D. C.

HELIUM

(Synonym: Helium-4)
(Formula: ^4He)

PHYSICAL PROPERTIES (1)

Atomic Mass	
Atomic Weight	0.004 002 6 kg
One Mole of ^4He	0.004 002 6 kg
Specific Volume @ 21.1 °C, 101.325 kPa	6 030.4 dm^3/kg; 96.6 ft^3/lb
Boiling Point @ 101.325 kPa	4.214 4 °K; −268.94 °C; −452.1 °F
Melting Point @ 2 555 kPa	1.2 °K; −272.0 °C; −457.5 °F
Lambda Point, Upper	
Temperature	2.173 °K; −271.0 °C; −455.8 °F
Pressure	5.07 kPa; 50.7 mbar; 38.0 mmHg
Lambda Point, Lower	
Temperature	1.760 °K; −271.4 °C; −456.5 °F
Pressure	3 003 kPa; 30.03 bar; 29.64 atm
Critical Temperature	5.20 °K; −268.0 °C; −450.3 °F
Critical Pressure	229 kPa; 2.29 bar; 33.2 psia; 2.261 atm
Critical Volume	14.431 dm^3/kg
Critical Density	0.069 3 kg/dm^3
Critical Compressibility Factor	0.305
Latent Heat of Fusion @ 1.2 °K, 2 555 kPa	0.334 7 J/mol; 0.08 cal/mol
Absolute Density, Gas @ 101.325 kPa @ 0 °C	0.178 5 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 0 °C (Air = 1)	0.138
Density, Liquid @ Saturation Pressure @ 2.173 °K	0.146 57 kg/l
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	20.967 J/(mol·°K)
@ Constant Volume	12.863 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.63
Viscosity, Gas @ 101.325 kPa @ 26.8 °C	0.020 12 mPa·s; 0.020 12 cP
Viscosity, Liquid, Helium I @ 3.0 °K	0.003 3 mPa·s; 0.003 3 cP
Viscosity, Liquid, Helium II @ 1.2 °K	0.001 89 mPa·s; 0.001 89 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 0 °C	0.141 84 W/(m·°K); 345.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid, Helium I @ 2.4 K	0.018 83 W/(m·°K); 45.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 1.0 °K	0.347 mN/m; 0.347 dyn/cm
Solubility In Water @101.325 kPa (partial pressure of helium) @ 20 °C	8.61 cm^3/1 kg water
Sonic Velocity	
Gas @ 0 °C, 101.325 kPa	96.99 m/s
Liquid @ 4.00 °K	190 m/s
Refractive Index, Gas @ 101.325 kPa, n_D @ 25 °C	1.000 031 97
Dielectric Constant, Gas @ 101.325 kPa @ 25 °C	1.000 063 9
First Ionization Potential	3.939 × 10^{-18} J; 24.586 eV
Minimum Excitation Energy	3.175 × 10^{-18} J; 19.818 eV

Description

Helium is a colorless, odorless and tasteless gas at room temperature and atmospheric pressure. It is present in dry air in a concentration of 5.24 ppm by volume. Its principal source in the United States is from certain natural gas wells in which the natural gas may contain up to 9% helium.

Helium is normally supplied as a nonliquefied gas compressed into cylinders at a pressure of 17 170 kPa (2 490 psig) at 21.1 °C. It is available in other size cylinders at lower pressures. It can also be obtained in size 1H cylinders at a pressure of 24 130 kPa (3 500 psig) at 21.1 °C.

Helium cannot be solidified merely by cooling the saturated liquid to absolute zero of temperature (0 °K). It has no triple point. To solidify helium at 0 °K, a considerable pressure about 25 atm (2 530 kPa) must be applied. Helium undergoes a transition at 2.173 °K (lambda point) from a more or less normal liquid to another having unique properties. The liquid at temperatures above 2.173 °K is called helium I and the liquid below this temperature is called helium II. Helium II is a superfluid and possesses zero entropy, extremely large thermal conductivity, and zero viscosity.

Specifications

Five grades of helium are supplied by Matheson.

1. Research Purity Grade

This grade of helium is of very high purity (99.999 9 mole % min.) and can be obtained from Matheson in small cylinders or Pyrex liter flasks.

2. Matheson Purity Grade

This grade of helium has a minimum purity of 99.999 9 mole %.

3. Ultra High Purity Grade

This grade of helium has a minimum purity of 99.999 mole %.

4. Zero Gas Grade

This grade of helium is certified to contain less than 0.5 ppm hydrocarbons as CH_4.

5. High Purity Grade

This grade of helium has a minimum purity of 99.995 mole %.

Uses

Helium is used extensively in the welding industry as an inert shielding gas for arc welding. It is also extensively used in the field of cryogenics. It is used in mixtures with neon and argon for electronic tubes and the familiar neon signs.

Helium has been used extensively in large balloons for upper atmosphere and cosmic ray studies. Small helium balloons are used by weather forecasters to carry meteorological instruments. Helium is used in the missile industry to pressurize rocket fuels and force them into rocket engines.

Helium is used considerably in laboratory and research operations, e.g., as a leak detector, in "dry boxes", as a temperature standard (helium gas thermometer), as a carrier in gas chromatography, etc.

Gas mixtures of helium and hydrocarbons are used as self-quenching fill gases for nuclear counters.

A mixture of helium and oxygen finds use as a breathing gas for divers who must work under high pressures. Atmospheres containing helium are used for therapy and anesthesia of patients suffering from asthma or other obstructive conditions in the respiratory passages.

Toxicity

Helium is nontoxic but can act as an asphyxiant by displacing the necessary amount of air to support life.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Leak Detection

All fittings and joints suspected of leaks should be painted with soap water solution; leaks will be indicated by bubble formation. Matheson Leak Detectors Models 8016 and 8017, may also be used to detect leaks of helium.

Disposal of Leaking Cylinders

For disposal of leaking cylinders containing helium, see Appendix II-C.

Materials of Construction

Since helium is inert no special materials of construction are required. However, any piping or vessels containing helium should be adequately designed by competent engineers, using a safety factor conforming with the ASME code for pressure piping.

Cylinder and Valve Description

Helium is packaged in DOT approved, high pressure steel cylinders. The cylinder valve outlet designated as standard for helium by the Compressed Gas Association (CGA) has a 0.965 inch diameter internal thread, right-hand, accepting a bullet-shaped nipple. Matheson supplies this standard on all helium cylinders. This outlet is designated as connection No. 580 (see Figure 1). Lecture bottles have a special 5/16 inch-32 threads per inch, female valve outlet and a 9/16 inch-18 threads per inch, male dual valve outlet.

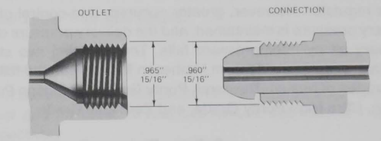


Fig. 1. CONNECTION 580 .965"-14 RH INT. accepting a Bullet Shaped Nipple

Safety Devices

Cylinders containing helium have safety devices of either the frangible disc type or frangible disc backed up with fusible metal, melting at approximately 100 °C. Cylinders pressurized 10% in excess of their marked service pressure in accordance with present DOT regulations must contain only safety devices of the unbacked frangible disc type. These safety devices are an integral part of the cylinder valve, situated opposite the valve outlet.

Recommended Controls

Automatic Pressure Regulators

In order to reduce the high cylinder pressure of helium to a safe working value consistent with a system's design, the following types of controls are recommended.

1. Single Stage Automatic Regulators

Single stage regulators will reduce cylinder pressure in one stage to a delivery pressure, in a particular range, depending upon the design of the regulator and its spring load. A single stage regulator will show a slight variation in delivery pressure as cylinder pressure falls. The following single stage regulators are available from Matheson for use with Research Purity Grade, Matheson Purity Grade, Ultra High Purity Grade, and Zero Gas Grade helium:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
19-580	28–340	0.28–3.4	4–50
3500-580	28–520	0.28–5.2	4–75

The following single stage regulators are available for use with High Purity Grade helium.

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
1L-580	28–550	0.28–5.5	4–80
1H-580	69–1 240	0.69–12.4	10–180
2-580	340–4 480	3.4–44.8	50–650
3-580	690–10 340	6.9–103.4	100–1 500
4-580	690–17 240	6.9–172.4	100–2 500
3320 (for lecture bottles only)	28–410	0.28–4.1	4–60

2. Two Stage Regulators

This type of regulator performs the same function as a single stage regulator. However, greater accuracy and control of the delivery pressure is maintained, and the delivery pressure does not vary as cylinder pressure falls. The following two stage regulators are available from Matheson for use with the following grades of helium: Research Purity Grade, Matheson Purity Grade, Ultra High Purity Grade, and Zero Gas Grade.

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
3800-580	28–620	0.28–6.2	4–90
3104-580	28–690	0.28–6.9	4–100

The following two stage regulators are available for use with High Purity Grade Helium:

Model No.	Deliver Pressure Range		
	kPa	bar (g)	psig
8L-580	14–104	0.14–1.04	2–15
8-580	28–340	0.28–3.4	4–50
8H-580	69–690	0.69–6.9	10–100
9-580	138–1720	1.38–17.2	20–250

3. Controls For Helium At Special High Pressure

High Purity Grade helium is also available at a special high pressure of 24 130 kPa (3 500 psig). The following single stage regulators are available for these cylinders.

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
3-580	690–10 340	6.9–103.4	100–1 500
4-580	690–17 240	6.9–172.4	100–2 500
3064-580	172–27 600	1.72–276.0	25–4 000*
3075-580	1 380–41 400	13.8–413.7	200–6 000*

Conventional equipment should never be used at this high pressure.

4. Low Pressure Regulator

The above regulators are not satisfactory for accurate delivery pressures below 34.5 kPa (5 psig). Therefore, an auxiliary regulator specifically designed for low pressures is recommended to be used in series where any of the standard type regulators having maximum delivery pressures up to 1 720 kPa (250 psig). Matheson has various models known as the Model 70 regulators which may be obtained with delivery pressures ranging from 0.5 kPa (2 inches water column) to 68.9 kPa (10 psig) as follows:

For low pressure regulation, Matheson supplies the following regulators with delivery pressure ranging from 2" water column to 69 kPa (10 psig):

Model No.	Delivery Pressure Range		
	kPa	mbar (g)	psig
70B	0.5–3.0	5–30	2–12 inches water column
70	3.4–34.5	34–345	0.5–5.0 psig
70A	34.5–68.9	345–689	5–10 psig

When these regulators are supplied to be used in conjunction with a standard regulator, an extra heavy hose is available to connect to the standard regulator. All Matheson regulators are provided with needle valves so that accurate flow control can be maintained.

A low pressure High Purity Regulator Model No. 71-S with stainless steel diaphragm, for use in series with Model 3500-580 regulator, is recommended for use in high purity applications. It has a delivery range of 3.5–41 kPa (0.5–6.0 psig).

Manual Controls

Manual needle valves for direct attachment to the cylinder valve outlet are available. These types of controls are mainly used where intermittent flows are necessary, or where it is desired to control the flow of gas directly from the cylinder. This type of a needle valve will allow control of extremely slow flow rates on up to relatively large flow rates. However, pressure cannot be controlled with such a valve, and, if a line or system becomes plugged, dangerous pressures can build up.

* Actual delivery pressure will be limited to cylinder gas pressure.

The following manual type valves are recommended for use with High Purity Grade helium: Model 50-580 or Model 52-580 with gauge to indicate tank pressure. The valves are normally supplied with hose connection, ¼" tube fittings or ¼" NPT male or female outlets. A Model 30AR or 31B needle valve is recommended for use with lecture bottles.

Model No. 4351-580 is recommended as a manual control for Matheson Purity, Research Purity and Ultra-High Purity helium.

Flowmeters

Matheson Series 7600 laboratory brass or stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass or stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Helium is shipped in high pressure steel cylinders as a nonflammable compressed gas, taking a DOT "Green Label". They are usually filled to a maximum of 10% in excess of the marked service pressure of the cylinder in accordance with present DOT regulations.

Commercial Preparations

The primary source of helium is from natural gas wells. It is obtained by a liquefaction and stripping operation. A new process for recovering helium utilizes the diffusion of helium through quartz. Helium is also obtained in small quantities from the air by liquefaction, rectification, and selective adsorption on charcoal at low temperatures.

Chemical Properties

Helium is a monatomic chemically inactive gas. It will not react with other elements or compounds under ordinary conditions.

Thermodynamic and Detailed Physical Data

Vapor Pressure (2)

Vapor pressure of helium from 0.5 °K to 5.2 °K (critical point) is shown below:

Temperature, °K	Vapor Pressure		
	kPa	mbar	mmHg
0.5	0.000 002 2	0.000 022	0.000 016 3
0.6	0.000 037 5	0.000 375	0.000 281
0.8	0.001 52	0.015 2	0.011 4
1.0	0.016 0	0.160	0.120
1.2	0.083 3	0.833	0.625
1.4	0.287	2.87	2.155
1.6	0.759	7.59	5.69
1.8	1.66	16.6	12.47
2.0	3.17	31.7	23.77
2.2	5.40	54.0	40.47
2.4	8.44	84.4	63.30
2.6	12.50	125.0	93.73
2.8	17.72	177.2	132.95
3.0	24.27	242.7	182.07
3.2	32.30	323.0	242.27
3.4	41.95	419.5	314.70
3.6	53.39	533.9	400.47
3.8	66.75	667.5	500.69
4.0	82.20	822.0	616.54
4.2	99.90	999.0	749.33
4.4	120.00	1 200.	900.26
4.6	142.8	1 428.	1 071.03
4.8	168.4	1 684.	1 263.21
5.0	197.1	1 971.	1 478.54
5.2	229.2	2 292.	1 718.82

Latent Heat of Vaporization, ΔHv

See Table 1 for ΔHv values.

Thermodynamic Data

For the thermodynamic properties of the saturated liquid and vapor and for those of real gas helium, see Tables 1 and 2, respectively.

Thermodynamic Properties of Helium As Ideal Monatomic Gas @ 25 °C (4)

Heat Capacity, C_p°	20.786 J/(mol·°K)
Entropy, S°	126.048 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_0^\circ)/298$	−105.262 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	6.198 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of helium, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] *Argon, Helium and the Rare Gases*, G. A. Cook, editor, *1961, Volume 1*, p. 324, Interscience Publishers, New York, New York.

[3] *Compressed Gas Handbook*, J. S. Kunkle, S. D. Wilson, and R. C. Cota, editors, *1969*, p. 514, NASA SP-3045, U. S. Government Printing Office, Washington, D. C.

[4] See reference 2, p. 293.

[5] *Technology of Liquid Helium*, R. H. Kropschat, B. W. Birmingham, and D. B. Mann, editors, Natl. Bur. Stand. Monograph 111, *1968*, p. 41, U. S. Government Printing Office, Washington, D. C.

[6] S. W. Akin, **Trans.** *Amer. Soc. Mech. Engrs.* 72, 751–757 (1950).

Table 1. THERMODYNAMIC PROPERTIES OF THE SATURATED LIQUID AND VAPOR (5)

Pressure kPa	Pressure atm	Temperature, °K	Entropy J/(mol·°K) Liquid	Entropy J/(mol·°K) Vapor	Enthalpy J/mol Liquid	Enthalpy J/mol Vapor	Heat of Vaporization J/mol	Specific Volume cm^3/mol Liquid	Specific Volume cm^3/mol Vapor	Density kg/dm^3 Liquid	Density kg/dm^3 Vapor
24.419	0.241	3.00	9.430	41.015	21.214	115.915	94.701	28.359	897.02	0.141 1	0.004 46
32.424	0.320	3.20	10.115	39.670	23.415	117.997	94.582	28.758	699.77	0.139 2	0.005 71
42.151	0.416	3.40	10.767	38.449	25.897	119.798	93.901	29.229	555.16	0.136 9	0.007 20
53.601	0.529	3.60	11.539	37.312	28.739	121.439	92.700	29.775	446.21	0.134 4	0.008 97
66.976	0.661	3.80	12.244	36.107	31.741	122.440	90.699	30.406	362.24	0.131 6	0.011 04
82.479	0.814	4.00	13.028	34.967	35.263	122.960	87.697	31.134	295.63	0.128 6	0.013 53
100.312	0.990	4.20	13.849	33.794	39.426	123.240	83.814	31.975	242.60	0.125 2	0.016 49
120.577	1.190	4.40	14.706	32.621	43.868	122.680	78.812	32.943	199.33	0.121 5	0.020 08
143.578	1.417	4.60	15.690	31.400	49.352	121.359	72.007	34.210	162.97	0.117 0	0.024 55
169.415	1.672	4.80	16.763	29.911	55.556	118.037	62.481	36.157	131.57	0.110 7	0.030 42
198.496	1.959	5.00	18.404	28.018	64.042	112.153	48.111	39.787	102.75	0.100 6	0.038 95

Table 2. THERMODYNAMIC PROPERTIES OF REAL GAS HELIUM (6)

V, Volume, cm^3/mol; **S**, Entropy, J/(mol·°K); **H**, Enthalpy, kJ/mol

Pressure kPa	Pressure atm		Temperature, °K 33.15	88.71	144.26	199.82	255.37	310.93	366.48	422.04	477.59	533.15
101.325	1.000	H	0.715 5	1.869 2	3.024 8	4.179 5	5.334 2	6.488 8	7.643 6	8.798 2	9.955 7	11.109 4
		S	67.741	88.356	98.521	105.337	110.479	114.582	118.015	121.046	123.558	125.852
		V	2 728.6	7 296.3	11 859.0	16 421.7	20 981.9	25 537.2	30 109.9	34 657.6	39 230.3	43 803.0
345	3.402	H	0.713 6	1.871 1	3.027 6	4.182 3	5.337 0	6.491 6	7.646 4	8.801 9	9.955 7	11.109 4
		S	57.525	78.157	88.339	95.155	100.297	104.400	107.833	110.780	113.376	115.670
		V	805.8	2 152.2	3 493.2	4 835.1	6 186.9	7 518.7	8 858.0	10 199.9	11 539.2	12 881.0
1 034	10.207	H	0.706 2	1.877 6	3.370 0	4.190 7	5.346 3	6.500 9	7.655 7	8.810 3	9.965 0	11.118 7
		S	48.298	69.014	79.196	86.028	91.153	95.273	98.706	101.653	104.232	106.526
		V	273.4	724.9	1 172.7	1 620.2	2 067.5	2 513.7	2 961.0	3 408.3	3 855.6	4 302.8
2 758	27.218	H	0.704 3	1.892 5	3.054 6	4.212 1	5.367 7	6.523 3	7.678 0	8.832 7	9.983 6	11.137 4
		S	39.857	60.808	71.023	77.856	82.997	87.100	90.550	93.497	96.076	98.371
		V	108.5	278.9	447.3	615.4	783.4	951.0	1 118.9	1 286.6	1 454.3	1 621.9
4 137	40.827	H	0.701 5	1.904 6	3.070 4	4.228 8	5.385 3	6.540 9	7.695 7	8.850 3	10.002 2	11.156 0
		S	36.441	57.408	67.640	74.490	79.614	83.734	87.167	90.115	92.710	95.005
		V	76.3	189.7	302.1	414.3	526.5	638.4	750.1	862.1	973.8	1 085.7
6 205	61.241	H	0.697 8	1.922 2	3.093 7	4.254 9	5.412 3	6.567 9	7.722 7	8.877 3	10.030 1	11.183 9
		S	33.226	53.992	64.241	71.090	76.231	80.351	83.801	86.748	89.327	91.638
		V	55.2	130.2	201.4	280.4	355.1	429.8	504.5	579.0	653.7	728.1
10 342	102.069	H	0.699 6	1.958 5	3.141 1	4.306 0	5.470 9	6.621 9	8.707 1	8.931 3	10.086 0	11.239 7
		S	29.340	49.705	59.954	66.820	71.961	76.097	79.514	82.495	85.074	87.385
		V	38.5	82.7	127.9	173.0	217.9	262.9	307.6	352.6	397.3	442.0
17 237	170.114	H		2.019 1	3.220 3	4.391 6	5.553 8	6.711 3	7.866 9	9.021 5	10.179 0	11.332 8
		S		45.417	55.666	62.533	67.691	71.827	75.243	78.224	80.820	83.114
		V	27.5	54.1	81.2	108.4	135.5	162.5	189.5	216.5	243.4	270.4
27 579	272.183	H		2.112 1	3.339 3	4.521 0	5.686 8	6.846 2	8.002 7	9.157 4	10.309 3	11.463 0
		S		41.515	51.697	58.564	63.738	67.875	71.308	74.289	76.885	79.196
		V	22.5	37.7	54.7	72.0	89.0	105.9	122.9	139.7	156.7	173.4
41 368	408.274	H		2.233 1	3.497 5	4.693 1	5.864 6	7.026 7	8.181 4	9.341 6	10.486 1	11.639 8
		S		38.166	48.248	55.130	60.322	64.291	67.892	70.889	73.485	75.796
		V	17.5	28.5	40.0	51.2	62.7	74.2	85.7	97.0	108.2	119.7

HEXAFLUOROACETONE

(Synonyms: Hexafluoro-2-propanone; Perfluoroacetone)
(Formula: F_3CCOCF_3)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.166 023 kg
One Mole of F_3CCOCF_3	0.166 023 kg
Specific Volume @ 21.1 °C, 101.325 kPa	143.6 dm^3/kg; 2.3 ft^3/lb
Vapor Pressure @ 21.1 °C	603 kPa; 6.03 bar; 87.5 psia; 5.95 atm
Boiling Point @ 101.325 kPa	245.65 °K; −27.5 °C; −17.5 °F
Freezing Point	151.15 °K; −122.0 °C; −187.6 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	6.821 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	5.757
Density, Liquid @ Saturation Pressure @ 23.4 °C	1.323 kg/l
Critical Temperature	357.25 °K; 84.1 °C; 183.4 °F
Critical Pressure	2 840 kPa; 28.4 bar; 411.5 psia; 28.0 atm
Critical Volume	1.747 dm^3/kg
Critical Density	0.572 kg/dm^3
Critical Compressibility Factor	0.277
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.020 6 mPa·s; 0.020 6 cP

Description

At room temperature and atmospheric pressure, hexafluoroacetone is a colorless, nonflammable, hygroscopic gas which fumes when exposed to moist air. Hexafluoroacetone has a musty odor which becomes acrid in the presence of acidic impurities. Hexafluoroacetone is shipped as a liquefied gas under its own vapor pressure of 500 kPa (72.5 psig) at 21.1 °C.

Specifications

Hexafluoroacetone has a minimum purity of 99.5%. Typically the purity exceeds 99.9%.

Uses

Hexafluoroacetone is a highly reactive gas which will undergo some of the usual reactions of aliphatic ketones and in addition will combine with a variety of active hydrogen compounds to give substituted hydroxyl compounds. It can be used to prepare such diversified products as stable fluids, solvents, adhesives, monomers, copolymers, and agricultural and pharmaceutical compounds.

Effects in Man (2)

The major effect of acute exposure is lung irritation, which can lead to pulmonary edema. It is also irritating to the skin, eyes, nose and throat, since it reacts with moisture to form a highly acidic sesquihydrate (pH < 1.0).

Toxicity (2)

The approximate LC_{50} for albino rats is 900 ppm for a 0.5 hour exposure and 275 ppm for a 3 hour exposure. Respiratory impairment was evident at all levels of exposure in the rats. At the lethal level, rats developed, in addition, conjunctival hemorrhage and, at sublethal levels, showed pigmented secretion around the eyes and nose.

Marked cumulative effects on various organs were noted in rats subjected to 10 repeated 4-hour exposures to sublethal concentrations of hexafluoroacetone, with apparently specific effects on the testes of the exposed rats.

Odor is not a reliable warning property of dangerous concentrations of this gas.

Threshold Limit Value (TLV)

The 1979 ACGIH recommends a Threshold Limit Value (TLV) of 0.1 ppm (0.7 mg/m^3) for hexafluoroacetone.

First Aid Treatment (2)

Inhalation

Remove the victim to an uncontaminated atmosphere immediately. Give oxygen if breathing is labored. If breathing ceases, start artificial respiration at once, with simultaneous administration of oxygen. Summon medical aid as soon as possible.

Note To Physician

Observe for premonitory signs and symptoms of pulmonary edema.

Skin and Eye Contact

Wash the affected areas with copious quantities of water for at least 15 minutes. Remove contaminated clothing under a drenching shower of water. In case of eye contact, get medical attention as soon as possible.

Precautions in Handling and Storage

Personnel handling or using hexafluoroacetone should do so only in a well-ventilated area, preferably a hood with forced ventilation. Personnel who handle the gas should wear protective clothing such as rubber or plastic aprons, rubber gloves, and suitable gas-tight safety goggles. Instant-acting showers should be available in the event of an emergency. Special eye-washing fountains or similar equipment should be available for eye irrigation. Air-line or oxygen masks or self-contained breathing apparatus should be conveniently located for emergency use.

Suckback may cause a violent reaction within the cylinder and may lead to the formation of extremely corrosive conditions; to prevent suckback it is advisable to employ a check valve, vacuum break, or trap.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Although leaks of hexafluoroacetone in lines and equipment may be determined by means of moist blue litmus (the paper will turn pink), it is suggested that the apparatus to be used be pretested for leaks with *dry* compressed air on an inert gas such as nitrogen.

Disposal of Leaking Cylinders

Leaking cylinders containing hexafluoroacetone that cannot be corrected normally may be disposed of in the following manner. Attach an appropriate regulator with a long rubber hose connection to the cylinder. Move the cylinder to a hood or safe out-of-doors area and run the contents at a moderate rate into a container filled with a moderate amount of water. The solution is ready for disposal after neutralization with aqueous sodium hydroxide, or the hexafluoroacetone hydrate may be recovered from the solution by distillation.

When the cylinder is empty, close the cylinder valve, tag the cylinder as defective, and return it as per supplier's instructions, after informing the supplier of the defect.

Materials of Construction

All equipment to be used for hexafluoroacetone should be clean and *dry* since hexafluoroacetone hydrates readily in the presence of moisture leading to acidic conditions. Monel, nickel, inconel, stainless steel, copper, and glass- and Hastellory C-lined equipment are satisfactory for handling hexafluoroacetone. Stainless steel autoclaves and Hastelloy C-lined bombs are satisfactory for high pressure reactions, with copper tubing being used for transfer of liquid or gaseous hexafluoroacetone. At atmospheric pressure, polyethylene and rubber tubing have been used for flexible connections.

Cylinder and Valve Description

Hexafluoroacetone is shipped in steel cylinders, which comply with DOT specifications. They have a minimum service pressure of 3 310 kPa (480 psig).

The hexafluoroacetone cylinder valve outlet designated as the alternate standard by the Compressed Gas Association is valve outlet No. 660. This outlet has a thread size of 1.030 inches diameter and is right-hand with external threads. The mating connection seats on a flat washer. Figure 1 illustrates the valve outlet and mating connection used in this service.

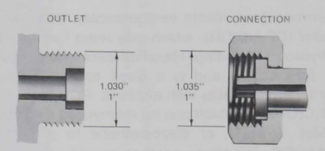


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

The lecture bottle containing one pound of hexafluoroacetone is 2 inches in diameter and 15 inches long and is equipped with a Teflon-packed monel valve having a special outlet designated as 5/16"-32 thread per inch, female outlet.

Safety Devices

Cylinders containing hexafluoroacetone have, as a safety device, a fusible metal plug, melting at approximately 73.9 °C (165 °F).

Recommended Controls

Automatic Pressure Regulator

Matheson supplies regulator Model B15-660, without cylinder pressure gauge, or Model B15C-660, with cylinder pressure gauge, for hexafluoroacetone service. This regulator has a chemically coated nickel body, with internal parts of monel. The diaphragm is Kel-F backed with silver plated nickel-silver alloy and the seat is of Kel-F. The needle valve on the outlet end is of monel. The delivery pressure range of the regulator is 28–340 kPa (4–50 psig).

To prevent suckback of foreign materials into the regulator, a monel check valve is recommended.

Manual Controls

A monel bar stock needle valve Model 55-660 can be supplied where noncritical manual flow control of the liquid or gas is required. This valve can be supplied with a serrated hose end, 1/4" compression fitting, or 1/4" NPT male or female pipe outlet. The lecture bottle utilizes a monel needle valve Model 33M or 60L.

Shipping Regulations

Hexafluoroacetone is classified as a nonflammable gas and is shipped under "Green Label."

Chemical Preparation

Hexafluoroacetone has been prepared by direct fluorination of acetone in the vapor phase over a copper wire screen packing, followed by fractionation of the mixture of products obtained. It has also been prepared by pyrolysis of poly(tetrafluoroethylene), followed by $KMnO_4$ oxidation of the mixture obtained, extraction with ether, distillation, and dehydration of the distilled hexafluoroacetone monohydrate over phosphorus pentoxide.

Chemical Properties

Hexafluoroacetone reacts exothermically with water giving the gem-diol $(CF_3)_2C(OH)_2$ which may react further with water through hydrogen bonding. Hexafluoroacetone sesquihydrate is acidic (pH < 1.0) and is a good solvent for polymers. Hexafluoroacetone reacts with alcohols, ROH, giving hemiketals $(CF_3)_2C(OH)OR$, which can be methylated with Me_2SO_4 + K_2CO_3, MeI + Ag_2O, or diazomethane to give the ketals $(CF_3)C(OMe)OR$. Hexafluoroacetone reacts with dry HCN in the presence of catalytic amounts of piperidine giving the cyanohydrin $(CF_3)_2C(OH)CN$, which on saponification with sulfuric acid yields $(CF_3)_2C(OH)CO_2H$. Condensation of hexafluoroacetone with cyanohydrins of aromatic aldehydes, RCH(OH)CN, gives 2,2-bis (trifluoromethyl)-5-aryl-4-oxazolidinones. Hexafluoroacetone reacts with hydroxylamine to form $(CF_3)_2C(OH)NHOH$. With primary amides, hexafluoroacetone forms addition compounds of the type $(CF_3)_2C(OH)NHCOR$. Hexafluoroacetone reacts with organic compounds containing active hydrogen atoms to give the corresponding adducts, e.g., with $CH_2(CO_2H)_2$, there is formed $(CF_3)_2C(OH)CH_2CO_2H$. Aromatic compounds react with hexafluoroacetone in the presence of Friedel-Crafts catalysts to give tertiary alcohols; e.g., with toluene, there is formed $4\text{-}CH_3C_6H_4C(CF_3)_2OH$. When phenol and hexafluoroacetone are heated at 100 °C. in the presence of HF in an autoclave, a bisphenol A derivative, $4\text{-}HOC_6H_4C(CF_3)_2C_6H_4OH\text{-}4$, is formed. Hexafluoroacetone reacts with olefins to form alkenols; e.g., with isobutylene, $(CH_3)_2CH{:}CH_2$, there is formed $(CF_3)_2C(OH)CH_2C(CH_3){:}CH_2$. Hydrogen halides, HX, react with hexafluoroacetone to form unstable adducts; e.g., with HCl, there is formed $(CF_3)_2C(OH)Cl$. Hexafluoroacetone reacts with hydrazoic acid, HN_3, to form $(CF_3)_2C(OH)N_3$. Alkali metal fluorides react with hexafluoroacetone to give alkoxides; e.g., with KF, there is formed $(CF_3)_2CF(OK)$, which reacts with acryloyl chloride to yield $CH_2{:}CHCO_2CF(CF_3)_2$, which can be polymerized. $(CF_3)_2CF(OK)$ reacts with epibromohydrin to give a dlycidyl ether, which can be polymerized. Hexafluoroacetone reacts with organometallic compounds, e.g., RMgX and HC:CNa, to give $(CF_3)_2CR(OH)$ and $(CF_3)_2C(OH)C{:}CH$, respectively. Hexafluoroacetone reacts with ketene to give 2,2-bis(trifluoromethyl)-2-propiolactone, which decomposes at 350 °C to form CO_2 and $(CF_3)_2C{:}CH_2$. The propiolactone can be converted by H_2SO_4 or $BF_3{\cdot}Et_2O$ into $(CF_3)_2C{:}CHCO_2H$. Pyrolysis of hexafluoroacetone at 550 °C. gives CO and hexafluoroethane while at 625 °C. trifluoroacetyl fluoride and difluoromethylene are formed initially, which give finally carbonyl fluoride, $(CF_3)_2C{:}CF_2$, and other products. Hexafluoroacetone has been converted to the semicarbazone, 2,4-dinitrophenylhydrazone, and hydrazone derivatives, the latter on oxidation with lead tetraacetate yielding the diazo compound $(CF_3)_2C{:}N_2$. Hexafluoroacetone has been reduced with lithium aluminum hydride or sodium borohydride or catalytically over copper-chromium oxide to $(CF_3)_2CHOH$. Other reactions of hexafluoroacetone are described by C. Woolf in the section on perchlorofluoroacetones in Kirk-Othmer's "Encyclopedia of Chemical Technology," 2nd Edition, Volume 9, pp. 754–767, 1966.

Thermodynamic and Detailed Physical Data

Molecular Structure

The hexafluoroacetone molecule has C_s symmetry, which implies that the two CF_3 groups are staggered with respect to each other (1). Structural parameters are as follows (1): bond distances: C—F 1.34 Å (1.34×10^{-10} m), C—C 1.52 Å (1.52×10^{-10} m), C═O 1.17 Å (1.17×10^{-10} m); bond angles: C—C—F 111.4°, C—C—C 116°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous hexafluoroacetone.

Vapor Pressure (3)

The vapor pressure of HFA between 233.15 °K and 257.25 °K is represented by the following equation:

$$\log_{10} P = 11.281\,636 - \frac{1\,813.956}{T} - 0.021\,491\,03T + (2.288\,914 \times 10^{-5}T^2)$$

in which P = atm and T = °K.

Some vapor pressure data calculated by this equation are shown below:

Temperature, °K	Vapor Pressure kPa	bar	atm
233.15	55.121	0.551	0.544
245.65	101.224	1.01	0.999
253.15	140.639	1.41	1.388
273.15	304.684	3.05	3.007
293.15	584.037	5.84	5.764
298.15	676.750	6.77	6.679
313.15	1 014.263	10.1	10.01
333.15	1 671.863	16.7	16.50
357.25 (C.T.)	2 840.140	28.4	28.03 (C.P.)

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv

Temperature, °C	ΔHv, kJ/kg
−50.0	141.869
−27.5	131.239
−13.0	124.677

Thermodynamic Data

Heat Capacity, Ideal Gas, C_p^o @ 25 °C	117.880 J/(mol·°K)

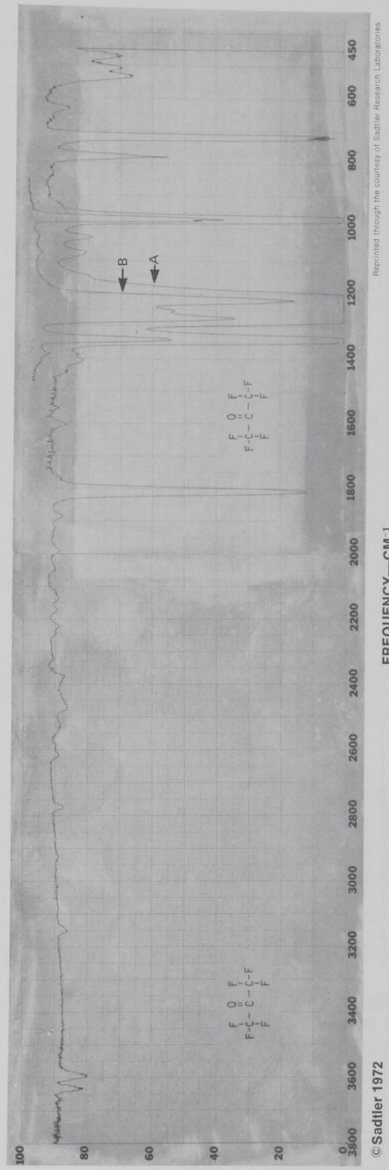


Fig. 2. Infrared spectrum of gaseous hexafluoroacetone over the frequency range 3 800–400 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure: curve A (complete scan): 2.66 kPa (20 mmHg); curve B (partial scan): 0.067 kPa (0.5 mmHg) (4).

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of hexafluoroacetone, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition 1977, pp. 57–60, Matheson, Lyndhurst, New Jersey.

[3] K. P. Murphy, *J. Chem. Eng. Data* 9, 259 (1964).

[4] *The Sadtler Standard Spectra, 1972*, The Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

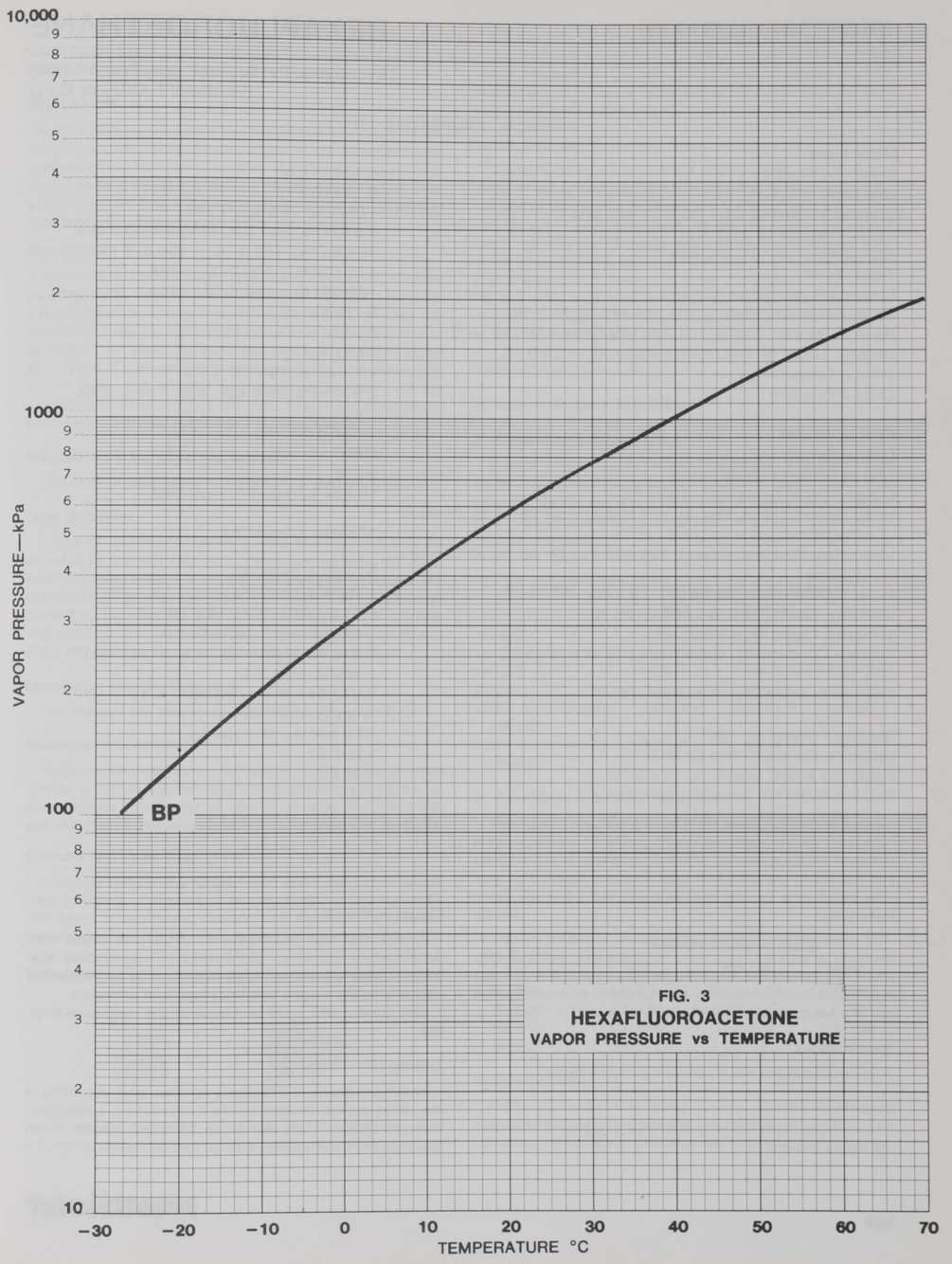


FIG. 3
HEXAFLUOROACETONE
VAPOR PRESSURE vs TEMPERATURE

HEXAFLUOROETHANE

(Synonyms: Perfluoroethane; Freon-116®)
(Formula: F_3CCF_3 or C_2F_6)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.138 012 kg
One Mole of C_2F_6	0.138 012 kg
Specific Volume @ 21.1 °C, 101.325 kPa	174.8 dm^3/kg; 2.8 ft^3/lb
Vapor Pressure @ 21.1 °C	3 070 kPa; 30.7 bar; 445 psia; 30.3 atm
Boiling Point @ 101.325 kPa	194.95 °K; −78.2 °C; −108.8 °F
Triple Point	173.10 °K; −100.0 °C; −148.1 °F
Freezing Point @ 101.325 kPa	172.55 °K; −100.6 °C; −149.1 °F
Absolute Density, Gas @ 101.325 kPa @ 23.9 °C	5.734 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 23.9 °C (Air = 1)	4.823
Density, Liquid @ Saturation Pressure@ − 80.0 °C	1.611 kg/l
Critical Temperature	292.85 °K; 19.7 °C; 67.5 °F
Critical Pressure	2 980 kPa; 29.8 bar; 432.1 psia; 29.4 atm
Critical Volume	1.644 8 dm^3/kg
Critical Density	0.608 kg/dm^3
Critical Compressibility Factor	0.278
Latent Heat of Fusion @ −100.6 °C	19.454 kJ/kg; 641.7 cal/mol
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	105.094 J/(mol·°K)
Molar Specific Heat, Gas @ 101.325 kpa @ 10 °C @ Constant Volume	92.385 J/(mol·°K)
Molar Specific Heat, Liquid @ −78.2 °C	131.29 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.014 4 mPa·s; 0.014 4 cP
Viscosity, Liquid @ −80°C	0.525 mPa·s; 0.525 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.016 15 W/(m·°K) 38.6 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −80 °C	0.012 544 W/(m·°K) 30.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −80 °C	17.2 mN/m; 17.2 dyn/cm
Dielectric Constant, Gas @ 23.0 °C	1.001 97
Refractive Index, Liquid, n_D −73.3 °C	1.206
Relative Dielectric Strength (N_2 = 1)	2.02

Description

At room temperature and atmospheric pressure, hexafluoroethane is an inert, colorless, nonflammable, nontoxic gas which is odorless and tasteless. Hexafluoroethane is shipped in cylinders or ton containers. It is reshipped as a nonliquefied gas at a pressure of 2 967 kPa (430 psig) at 21.1 °C.

Specifications

Hexafluoroethane has a minimum purity of 99.6%.

Uses

Hexafluoroethane is chiefly of interest as a propellant and as a gaseous insulator.

Effects in Man (2)

Inhalation of high concentrations of gas can cause such symptoms as dizziness, disorientation, incoordination, narcosis, nausea or vomiting. There appear to be no irreversible effects once the oxygen deficiency has been corrected.

Skin contact with liquid hexafluoroethane can cause frostbite.

Toxicity (2)

Hexafluoroethane is a relatively nontoxic gas, according to the rating system devised by the Underwriters' Laboratory, Chicago, Illinois. It falls into Group 5A in this system, which also includes the relatively nontoxic carbon dioxide.

Matheson

First Aid Treatment

INHALATION

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration and oxygen simultaneously. Treat symptomatically thereafter.

Skin Contact

In case of skin contact with liquid hexafluoroethane, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Leak Detection

Leaks of hexafluoroethane in lines or equipment may be detected by painting the sites of the suspected leaks with soap water solution; leaks will be evident by bubble formation. Minute leaks in pressurized equipment filled with hexafluoroethane may be detected with either a halide torch or a halide leak detector. The Matheson Leak Detector Models 8016 and 8017 provide a more sensitive means of leak detection.

Disposal of Leaking Cylinders

For disposal see procedure described in Appendix II-C.

Materials of Construction

Since hexafluoroethane is noncorrosive, any of the common structural metals may be used under ordinary conditions. At temperatures of the order of 150 °C, copper, stainless steel, and aluminum are resistant to attack by decomposing products.

Cylinder and Valve Description

Hexafluoroethane is shipped in DOT approved, high pressure steel cylinders. Cylinders of hexafluoroethane are equipped with brass valves having the alternate standard Compressed Gas Association (CGA) valve outlet connection No. 320. The valve outlet has a thread size of 0.825", with right-hand internal threads, with a flat seat using a washer as a seal (see Figure 1 for an illustration). Lecture bottles have a special 5/16"-32 threads per inch, female outlet and a 9/16"-18 threads per inch male, dual valve outlet.

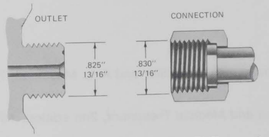


Fig. 1. CONNECTION 320 .825"-14 RH EXT. used with Flat Seat and Washer

Safety Devices

Cylinders of hexafluoroethane are equipped with frangible discs as safety devices. The frangible disc is required in only one end of the cylinder regardless of the length of the cylinder. Cylinders of hexafluoroethane should, therefore, be stored away from sources of heat to avoid dangerous pressures from developing within the cylinder. Frangible discs backed up with fusible metal plugs, melting at about 73.9 °C (165 °F) or 100 °C (212 °F), may also be used as safety devices, but in cylinders over 55 inches long, exclusive of the neck, this device is required in both ends.

Recommended Controls

Automatic Pressure Regulators

1. Single Stage Regulators

A single stage regulator will reduce cylinder pressure in one stage to a delivery pressure in a particular range, depending upon the design of the regulator and its spring load. A single stage regulator will show a variation in delivery pressure as cylinder pressure falls. The following Matheson single stage regulators are recommended for use with hexafluoroethane.

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
1P-320	28–240	0.28–2.4	4–35
1L-320	28–550	0.28–5.5	4–80
1H-320	69–1 240	0.69–12.4	10–180
2-320	345–4 480	3.45–44.8	50–650
3320 (with lecture bottles)	28–410	0.28–4.1	4–60
3321 (with lecture bottles)	0.28–4.1	28–410	4–60

2. Two Stage Automatic Regulators

This type of regulator performs the same function as a single stage regulator. However, greater accuracy in control of delivery pressure is maintained and the delivery pressure does not vary as cylinder pressure falls. The following Matheson two stage regulators are recommended for use with hexafluoroethane:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
8L-320	14–104	0.14–1.04	2–15
8-320	28–340	0.28–3.4	4–50
8H-320	69–690	0.69–6.9	10–100
9-320	138–1720	1.38–17.2	20–250

Manual Controls

Matheson needle valve Model 50-320, of brass bar stock, is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets (¼" compres-

Matheson

sion or ¼" NPT male or female pipe) but it is usually supplied with a serrated hose end. It should be used only where manual flow control is needed and should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. Needle valve No. 31B is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass flowmeter units with 65 mm tubes with single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Hexafluoroethane is classified by the DOT as a nonflammable compressed gas and is shipped with the required "Green Label."

Chemical Preparation

Hexafluoroethane has been obtained in almost quantitative yields by fluorination of ethane with diluted fluorine under "cool-flame" conditions.

Chemical Properties

Hexafluoroethane is among the most stable of organic compounds. Reaction with quartz does not occur below approximately 600 °C and homogeneous decomposition is not appreciable at 842 °C.

Thermodynamic and Detailed Physical Data

Molecular Structure (1)

Hexafluoroethane has D_{3d} symmetry and a symmetry number of 6, with C—F and C—C bond distances of 1.32 Å (1.32×10^{-10} m) and 1.56 Å (1.56×10^{-10} m), respectively, and a C—C—F bond angle of 109.5 ± 1.5°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous hexafluoroethane.

Vapor Pressure (3)

Temperature, °K	Vapor Pressure kPa	bar	mmHg
173.15	28.3	0.283	212.0
193.15	93.1	0.931	698.1
213.15	24.5	2.45	1 835.9

For vapor pressure data from 223.15 °K to 292.85 °K, see Figure 3 (vapor pressure vs. temperature curve).

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/kg
183.15	121.3
194.95	117.03
203.15	113.0

Thermodynamic Properties of Hexafluoroethane As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	106.407 J/(mol·°K)
Entropy, S°	332.076 J/(mol·°K)
Free Energy Function, $(G_{298}^\circ - H_{298}^\circ/298$	−332.076 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	20.255 kJ/mol
Enthalpy of Formation, ΔH_f°	−1 343.901 kJ/mol
Gibbs Energy of Formation, ΔG_f°	−1 258.212 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of hexafluoroethane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, 1975, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, 1977, pp. 119–123, Matheson, Lyndhurst, New Jersey.

[3] "*Freon*" *Fluorocarbons*, Tech. Bull. B-2, 1964, E. I. duPont de Nemours & Co., Inc., Wilmington, Delaware.

[4] *JANAF Thermochemical Tables*, 2nd edition, 1971, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[5] **The Sadtler Standard Spectra**, 1972, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[6] "*Freon*" *Tech. Bull. EL-15, 1969*, E. I. duPont de Nemours & Co., Inc., Wilmington, Delaware.

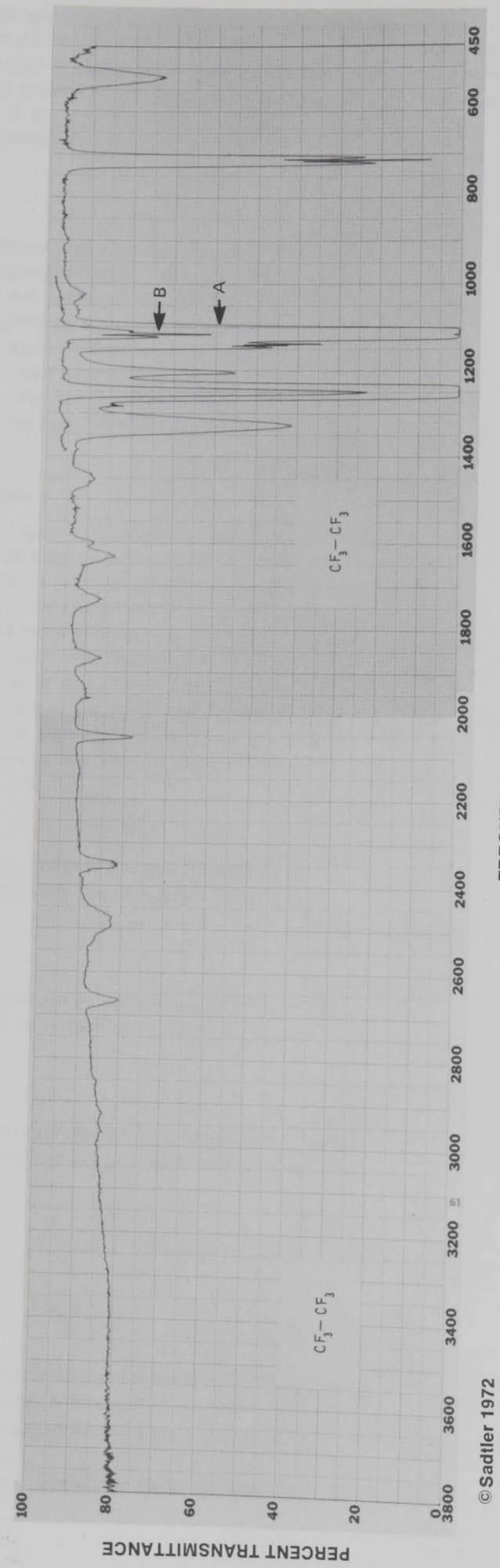


Fig. 2. Infrared spectrum of gaseous hexafluoroethane over the frequency region of 3 800 cm^{-1} to 450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure: curve A (complete scan): 2.666 kPa (20 mmHg), curve B (partial scan): 0.067 kPa 0.667 mbar (0.5 mmHg) (5).

Matheson

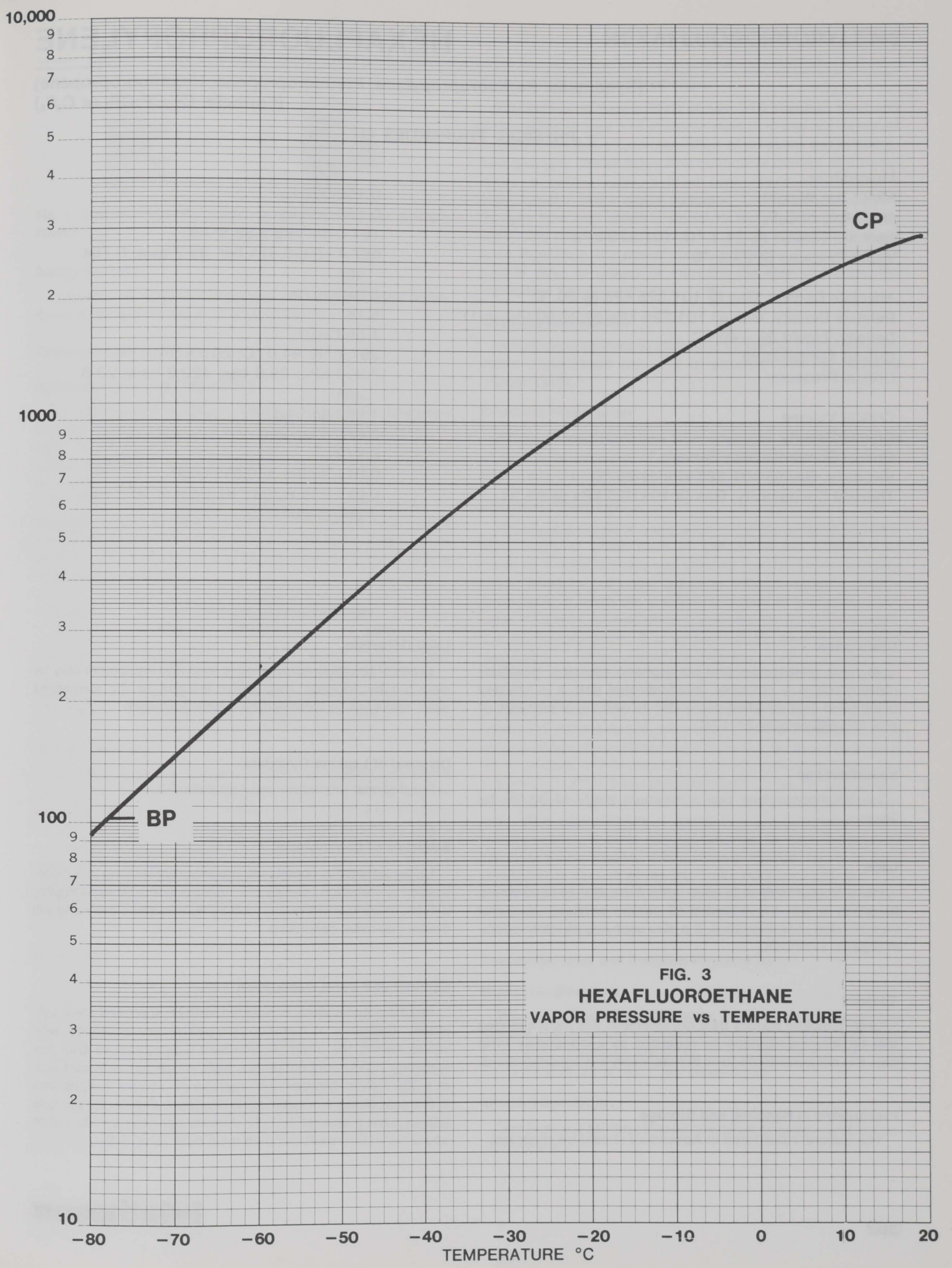


FIG. 3
HEXAFLUOROETHANE
VAPOR PRESSURE vs TEMPERATURE

HEXAFLUOROPROPYLENE

(Synonyms: Perfluoropropylene; Perfluoropropene; Hexafluoropropene)
(Formula: $CF_3CF{:}CF_2$ or C_3F_6)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.150 023 kg
One Mole of C_3F_6	0.150 023 kg
Specific Volume @ 21.1 °C, 101.325 kPa	161.0 dm^3/kg 2.58 ft^3/lb
Vapor Pressure @ 21.1 °C	687.4 kPa; 6.874 bar; 99.7 psia; 6.784 atm
Absolute Density, Gas @ 101.325 kPa @ 20 °C	6.240 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	5.18
Density, Liquid @ −40 °C	1.583 kg/l
Critical Temperature	367.1 °K; 94.0 °C; 201.1 °F
Critical Pressure	2 900 kPa; 29.0 bar; 420.3 psia; 28.6 atm
Critical Volume	1.959 dm^3/kg
Critical Density	0.510 4 kg/dm^3
Critical Compressibility Factor	0.279
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.011 9 mPa·s; 0.011 9 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.011 255 W/(m·°K); 26.9×10^{-6} cal·cm/(s·cm^2·°C)

Description

At room temperature and atmospheric pressure, hexafluoropropylene is a colorless, nonflammable gas. It is shipped uninhibited as a liquefied gas under its own vapor pressure of 586 kPa (85 psig) at 21.1 °C.

Specifications

Hexafluoropropylene has a minimum purity of 99.5% by volume.

Uses

Hexafluoropropylene is used in the formation of copolymers to which it has the potential of adding nonflammable and nonoxidizing characteristics. It is also useful as an intermediate in organic synthesis.

Toxicity

Until complete toxicity data are available, it is recommended that hexafluoropropylene be regarded as a moderately toxic gas. It is not considered toxic in reasonably low concentrations.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Leak Detection

Leaks of hexafluoropropylene in lines and equipment may be detected by applying soap water solution to the suspected sites; leaks will be indicated by bubble formation.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-C.

Materials of Construction

Under anhydrous conditions, hexafluoropropylene is not corrosive to common metals of construction. Hexafluoropropylene, in contact with water, will be hydrolyzed slowly and will create corrosive conditions.

Cylinder and Valve Description

Hexafluoropropylene is shipped in DOT approved steel cylinders. Cylinders of hexafluoropropylene are equipped with valves having the alternate standard Commpressed Gas Association (CGA) connection No. 660, which has a thread size of 1.030 inches diameter, with right-hand external threads with a flat seat using a washer as a seal (see Figure 1). Lecture bottles have a special 5/16"-32 threads per inch female outlet and a 9/16"-18 threads per inch male dual valve outlet.

Matheson

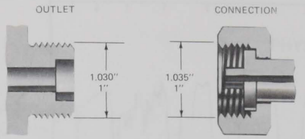


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders of hexafluoropropylene have fusible metal safety devices, melting at about 73.9 °C (165 °F).

Recommended Controls

Automatic Pressure Regulators

For satisfactory automatic pressure regulation, Matheson supplies single stage automatic pressure regulator Model 1P-660. This regulator has an aluminum body and neoprene rubber diaphragm. It has a delivery pressure range of 28-240 kPa (4-35 psig).

For low pressure regulation Matheson supplies a Model 70 regulator, which is constructed of an aluminum body and a Buna N diaphragm. It has an oversized pancake body to allow sensitive and accurate low pressure control. Three pressure ranges are available:

Model No.	Delivery Pressure Range kPa	mbar (g)	psig
70B-660	0.5–3.0	5–30	2–12 inches water column
70-660	3.4–34.5	34–345	0.5–5.0 psig
70A-660	34.5–68.9	345–689	5–10 psig

Manual Controls

Manual needle valve Model 50-660 is available for direct attachment to the cylinder valve outlet. This valve can be equipped with a variety of outlets, (¼" compression fitting or ¼" NPT male or female pipe) but is usually supplied with a serrated hose end. It should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged, or if the system itself is closed. Matheson needle valve Model 31B is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass flowmeter units with 65 mm tubes with a single float, of the rotameter type, are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, much as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Hexafluoropropylene is classified by the DOT as a nonflammable compressed gas and is shipped with the required "Green Label."

Chemical Preparation

Hexafluoropropylene has been prepared by decomposition of Teflon, by pyrolysis of chlorodifluoromethane, and by debromination of 1,2-dibromohexafluoropropane.

Chemical Properties

Hexafluoropropylene undergoes a variety of addition reactions, many of which have no parallel in the chemistry of ethylene. It adds bromine and chlorine readily at room temperature. When heated under pressure with 5% aqueous hydrofluoric acid, it forms the low-boiling isomer of heptafluoropropane. Antimony pentafluoride fluorinates hexafluoropropylene into perfluoropropane. It is epoxidized by alkaline hydrogen peroxide to 1,2-epoxyhexafluoropropane. It adds alcohols; for example, with methanol it forms 1-methoxy-1,1,2,3,3,3-hexafluoropropane. It adds hydrogen bromide; at 200 °C in the presence of activated carbon and calcium sulfate, it forms 1-bromo-1,1,2,3,3,3-hexafluoropropane, while irradiation of a mixture of hexafluoropropylene and hydrogen bromide gives a 43:57 mixture of 2-bromo-1,1,2,3,3,3-hexafluoropropane and 1-bromo-1,1,2,3,3,3-hexafluoropropane. It reacts with aluminum chloride to give a variety of chlorinated substitution products. With phenyllithium it forms (1,2,3,3,3-pentafluoropropenyl)benzene. It adds nitrosyl chloride to form 1-chloro-2-nitrohexafluoropropane. When heated to 200 °C. It is converted into a mixture of cis and trans perfluoro-1,2- and 1,3-dimethylcyclobutanes. It acts as a dienophile and forms adducts with butadiene, cyclopentadiene, and anthracene. It adds carbonyl fluoride to form perfluoroisobutyryl fluoride.

Thermodynamic and Detailed Physical Data

Molecular Structure

Electron diffraction and Raman and infrared spectroscopy indicate the hexafluoropropylene molecule to be linear, with C—C and C═C bond distances of 1.52 Å (1.52×10^{-10} m) and 1.31 Å (1.31×10^{-10} m), respectively.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous hexafluoropropylene.

Matheson

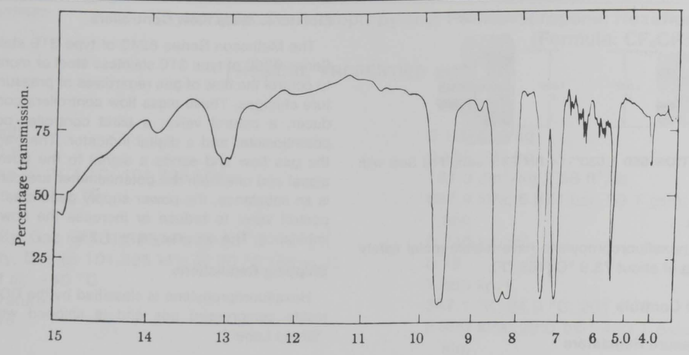


Fig. 2. Infrared spectrum of gaseous hexafluoropropylene (3).

Vapor Pressure (2)

Temperature, °K	Vapor Pressure kPa	bar	mmHg
232.45	61.727	0.62	463
237.59	79.591	0.80	597
243.04	102.521	1.03	769
248.32	128.389	1.28	963
257.28	187.046	1.87	1 403
264.85	251.843	2.52	1 889
269.85	303.033	3.03	2 273
275.10	369.431	3.69	2 771
280.15	439.021	4.39	3 293
285.25	515.552	5.16	3.867
292.90	652.746	6.53	4 896

Latent Heat of Vaporization, ΔHv @ −29.6	134.503 kJ/kg; 4 822.8 cal/mol
Thermodynamic Data	
Heat Capacity, Ideal Gas, O_p^o @ 25 °C	116.283 J/(mol·°K)

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of hexafluoropropylene, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] G. H. Whipple, *Ind. Eng. Chem.* 44, 1664 (1952).

[3] E. G. Young and W. S. Murray, *J. Amer. Chem. Soc.* 70, 2814 (1948).

(Formula: H_2)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.002 016 kg
One Mole of H_2	0.002 016 kg
Specific Volume @ 21.1 °C, 101.325 kPa	11 967.4 dm^3/kg; 191.7 ft^3/lb
Boiling Point, Normal H_2 @ 101.325 kPa	20.384 °K; −252.8 °C; −423.0 °F
Boiling Point, 20.4 °K Equilibrium H_2 @ 101.325 kPa	20.267 °K; −252.9 °C; −423.2 °F
Triple Point, Normal H_2	
Temperature	13.95 °K; −259.2 °C; −434.6 °F
Pressure	7.075 kPa; 70.75 mbar; 53.0 mmHg
Triple Point, 20.4 °K Equilibrium H_2	
Temperature	13.83 °K; −259.3 °C; −434.8 °F
Pressure	7.04 kPa; 70.4 mbar; 52.8 mmHg
Absolute Density, Normal H_2 Gas @ 101.325 kPa @ 25 °C	0.082 35 kg/m^3
Relative Density, Normal H_2 Gas @ 101.325 kPa @ 25 °C (Air = 1)	0.069 5
Density, Saturated Liquid Normal H_2 @ 23 °K	67.723 kg/l
Density, Saturated Liquid Para H_2 @ 23 °K	67.477 kg/l
Critical Constants, Normal H_2	
Critical Temperature	33.24 °K; −239.9 °C; −399.8 °F
Critical Pressure	1 297 kPa; 12.97 bar; 188.1 psia; 12.80 atm
Critical Volume	32.242 dm^3/kg
Critical Density	0.031 0 kg/dm^3
Critical Compressibility Factor	0.305
Critical Constants, 20.4 °K Equilibrium H_2	
Critical Temperature	32.98 °K; −240.2 °C; −400.3 °F
Critical Pressure	1 294 kPa; 12.94 bar; 187.7 psia; 12.77 atm
Critical Volume	32.49 dm^3/kg
Critical Density	0.030 8 kg/dm^3
Critical Compressibility Factor	0.309
Latent Heat of Fusion, 20.4 °K Equilibrium H_2 @ 13.8 °K	58.16 kJ/kg; 13.90 kcal/kg; 25.02 Btu/lb
Flammability Limits In Air	4.0–75.0% (by volume)
Molar Specific Heat, Normal H_2 Gas @ 101.325 kPa @ 26.8 °C	
@ Constant Pressure	28.851 J/(mol·°K)
@ Constant Volume	20.535 J/(mol·°K)
Specific Heat Ratio, Normal H_2 Gas @ 101.325 kPa @ 26.8 °C, Cp/Cv	1.405
Viscosity, Gas, Normal H_2 @ 101.325 kPa @ 26.8 °C	0.008 957 mPa·s; 0.008 957 cP
Viscosity, Saturated Liquid, Normal H_2 @ 21 °K	0.012 84 mPa·s; 0.012 84 cP
Viscosity, Saturated Liquid, Para H_2 @ 21 °K	0.012 53 mPa·s; 0.012 53 cP
Thermal Conductivity, Gas, Normal H_2 @ 101.325 kPa @ 26.8 °C	0.181 699 W/(m·°K); 434.3×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid, Normal or Para H_2 @ 21 °K	0.120 8 W/(m·°K); 288.7×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension, Normal H_2 @ 20.38 °K	1.946×10^3 N/m
Surface Tension, Para H_2 @ 20.27 °K	1.930×10^3 N/m
Solubility In Water @ 101.325 kPa (partial pressure H_2) @ 20 °C	0.018 2 cm^3/1 cm^3 water
Autoignition Temperature	844.3 °K; 571.2 °C; 1 060 °F

HYDROGEN

Refractive Index, Normal H_2 Gas, n_D @ 20 °C and 101.325 kPa	1.000 129 7
First Ionization Potential	25.0×10^{-17} J; 15.6 eV
Dielectric Constant, Liquid @ 20.38 °K	1.230

Description

Hydrogen is a colorless, odorless, flammable gas and the lightest gas known. It is usually shipped as a nonliquefied gas in high pressure 1A cylinders at 15 170 kPa (2 200 psig) at 21.1 °C, at lower pressures in smaller cylinders and lecture bottles. Prepurified hydrogen is also available at 24 130 kPa (3 500 psig) at 21.1 °C.

The hydrogen atom, consisting of one proton and one electron, is the lightest and simplest atom. The electrons possess spin, and the hydrogen molecule is formed only from two hydrogen atoms containing electrons with opposed spins. The hydrogen molecules formed exist in two isomeric forms. One form is designated as orthohydrogen, in which the two atomic nuclei are spinning in the same direction (parallel spin); in the other form, designated as parahydrogen, the nuclear spins are opposed (antiparallel spin). At or above room temperature, the equilibrium composition is 75:25 ortho-para. Lowering the temperature favors the formation of the para form. Thus, at liquid nitrogen temperature (77.4 °K) the equilibrium is 52:48 ortho-para, and at the normal boiling point (20.4 °K), the equilibrium composition is 0.2:99.8 ortho-para.

When gaseous hydrogen is liquefied, the liquid hydrogen obtain has the 75:25 ortho-para ratio, and is referred to as normal hydrogen. When gaseous hydrogen is liquefied, the liquid hydrogen is slowly converted to the para form. This conversion occurs rapidly in the presence of certain catalysts. While it is possible to prepare essentially pure parahydrogen by equilibrating on a catalyst at very low temperatures, pure orthohydrogen cannot be made in the same manner. The isomers have, however, been separated by gas chromatography on activated Al_2O_3 columns at low temperatures, giving over 99% pure orthohydrogen.

Specifications

Six grades of hydrogen are supplied by Matheson, as follows:

1. Research Purity Grade

This grade of hydrogen is of the highest purity obtainable and is available in small cylinders and Pyrex liter flasks. It has a minimum purity of 99.999 9 mol %.

2. Matheson Purity Grade

This grade has a minimum purity of 99.999 9 mol %.

3. Ultra High Purity Grade

This grade has a minimum purity (on a helium-free basis) of 99.999 mol %.

4. Prepurified Grade

This grade is the purest commercial grade available. It has a minimum purity of 99.95 mol %. This grade is supplied in 1A cylinders at 15 170 kPa (2 200 psig), in smaller size cylinders at 13,790 kPa (2 000 psig), in lecture bottles at 12 240 kPa (1 775 psig), and also in very high pressure cylinders at 24 130 kPa (3 500 psig).

5. Zero Gas Hydrogen

This grade is certified to contain less than 0.5 ppm total hydrocarbons as methane.

6. Extra Dry Grade

This grade has a minimum purity of 99.9 mol %.

Uses

Hydrogen is widely used for the hydrogenation of vegetable and animal oils and fats. Hydrogen also finds wide use in the metallurgy field because of its ability to reduce metal oxides and prevent oxidation of metals in heat treating certain metals and alloys. Hydrogen finds some usage in the welding and cutting of metals. Hydrogen is extensively used in the synthesis of ammonia and in petroleum refining operations. Liquefied hydrogen has been used as a primary rocket fuel for combustion with oxygen or fluorine, and as a propellant for nuclear-powered rockets and space vehicles.

Toxicity

Hydrogen is nontoxic but can act as an asphyxiant by displacing the necessary amount of air required to support life.

Precautions in Handling and Storage

The major hazard associated with the handling of hydrogen is flammability. The following specific rules apply when handling hydrogen:

1. Never use cylinders of hydrogen in areas where flames, excessive heat, or sparks may occur.
2. Utilize only explosion proof equipment, and sparkproof tools in areas where hydrogen is handled.
3. Ground all equipment and lines used with hydrogen.
4. Never use a flame to detect hydrogen leaks—use soapy water.
5. Do not store reserve stocks of hydrogen with cylinders containing oxygen, other highly oxidizing or combustible materials.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks of hydrogen in lines and equipment may be detected with soapy water. Leaks will be indicated by bubble formation.

Disposal of Leaking Cylinders

Leaks in cylinders containing hydrogen which cannot be corrected normally can be disposed of by the procedure described in Appendix II-A.

Materials of Construction

Since hydrogen is noncorrosive, no special materials of construction are required. However, any piping or vessels containing hydrogen should be designed by competent engineers, using a safety factor conforming with the ASME code for pressure piping.

The handling of hydrogen at elevated pressures and temperatures poses serious equipment problems, since possible hydrogen embrittlement adds difficulties to normal equipment design.

Cylinder and Valve Description

Hydrogen is packaged in DOT approved, high pressure steel cylinders. The cylinder valve outlets designated as standard by the Compressed Gas Association (CGA) and the one used by Matheson, is a left-hand 0.825 inch diameter external thread accepting a round-shaped nipple, designated as No. 350 (see Figure 1). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet and a 9/16 inch-18 threads per inch male, dual valve outlet.

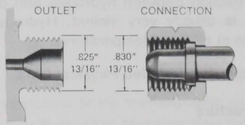


Fig. 1. CONNECTION 350 .825"-14 LH EXT. accepting Round Shaped Nipple

Safety Devices

Matheson cylinders containing hydrogen have safety devices of the frangible disc type backed up with fusible metal, melting at approximately 100 °C (212 °F). The safety device is an integral part of the cylinder valve, situated opposite the valve outlet.

Recommended Controls

Automatic Pressure Regulators

1. Single Stage Automatic Regulators

Single stage regulators will reduce cylinder pressure in one stage to a delivery pressure, in a particular range, depending upon the design of the regulator and its spring load. A single stage regulator will show a slight variation in delivery pressure as cylinder pressure falls. The following single stage regulators are available for use with Research Purity Grade Hydrogen, Ultra High Purity, Matheson Purity and Zero Gas hydrogen.

Model No.	Delivery Pressure Range kPa	bar (g)	psig
19-350	28–245	0.28–3.45	4–50
3500-350	28–520	0.28–5.2	4–75

The following single stage regulators are available for Prepurified Grade and Extra Dry Grade hydrogen.

Model No.	Delivery Pressure Range kPa	bar (g)	psig
1L-350	28–550	0.28–5.5	4–80
1H-350	69–1240	0.69–12.4	10–180
2-350	345–4480	3.45–44.8	50–650
3-350	690–10340	6.9–103.4	100–1 500
4-350	690–17240	6.9–172.4	100–2 500
3320 (for lecture bottles only)	28–410	0.28–4.1	4–60

The following single stage regulators are available for Prepurified Grade Hydrogen at 24 130 kPa (3 500 psig).

Model No.	kPa	bar (g)	psig
3-350	690–10 340	6.9–103.4	100–1 500
4-350	690–17 240	6.9–172.4	100–2 500
3064-350	172–27 600	1.72–276.0	25–4 000*
3075-350	1 380–41 370	13.8–413.7	200–6 000*

2. Two Stage Regulators

This type of regulator performs the same function as single stage regulators. However, greater accuracy and control of delivery pressure is maintained, and the delivery pressure does not vary as cylinder pressure falls. The following two stage regulators are available from Matheson: for use with Research Purity Grade Hydrogen, Ultra High Purity Grade, Matheson Purity and Zero Gas hydrogen:

Model No.	Delivery Pressure Range kPa	bar (g)	psig
3800-350	28–620	0.28–6.2	4–90
3104-350	28–690	0.28–6.9	4–100

The following two stage regulators area available for use with Prepurified Grade and Extra Dry Grade hydrogen:

Model No.	Delivery Pressure Range kPa	bar (g)	psig
8L-350	14–104	0.14–1.04	2–15
8-350	28–340	0.28–3.4	4–50
8H-350	69–690	0.69–6.9	10–100
9-350	138–1720	1.38–17.2	20–250

* Delivery pressure is dependent on cylinder gas pressure.

3. Low Pressure Regulators

The above regulators are not satisfactory for accurate delivery pressures below 34.5 kPa (5 psig). Therefore, an auxiliary regulator specifically designed for low pressures is recommended to be used in series with any of the standard type regulators having delivery pressures to 1 720 kPa (250 psig). Matheson has Model 70 regulators which may be obtained with delivery pressures ranging from 2 inches water column to 69 kPa (10 psig) as follows:

Model No.	Delivery Pressure Range		
	kPa	mbar (g)	psig
70B	0.5–3.0	5–30	2–12 inches water column
70	3.4–34.5	34–345	0.5–5.0 psig
70A	34.5–68.9	345–689	5–10 psig

When these regulators are supplied to be used in conjunction with a standard regulator, an extra heavy hose is available to connect to the standard regulator. All Matheson regulators are provided with needle valves so that accurate flow control can be maintained.

Low pressure regulator Model 71-S, with stainless steel diaphragm, for use with the Model 3500-350 regulator, is recommended for use with Ultra High Purity hydrogen. It has a delivery range of 3.5–41.4 kPa (0.5–6.0 psig).

Manual Controls

Manual needle valves for direct attachment to the cylinder valve outlet are available. These types of controls are mainly used where intermittent flows are necessary, or where it is desired to control the flow of gas directly from the cylinder. This type of needle valve will allow control of extremely slow flow rates on up to relatively large flow rates. However, pressure cannot be controlled with such a valve, and, if a line or system becomes plugged, dangerous pressures can build up. The following manual type valves are recommended for use with Prepurified Grade Hydrogen and Extra Dry Grade hydrogen: Model 50-350, and Model 52-350 with pressure gauge to indicate tank pressure. These values can be supplied with hose connection, ¼" tube fitting, or ¼" NPT male or female outlets. The Models 30AR or 31B is recommended for use with lecture bottles containing these grades of hydrogen.

Manual control Model 4351-350 is recommended for use with Research Purity Grade hydrogen, Ultra High Purity Grade, Matheson Purity and Zero Gas hydrogen.

Flowmeters

Matheson Series 7600 laboratory brass or stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass or stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Hydrogen is shipped in high pressure steel cylinders as a flammable compressed gas, taking a DOT "Red Gas Label." They are usually filled to the marked service pressure of the cylinder.

Commercial Preparations

Hydrogen may be commercially prepared by:

1. electrolysis of water which yields hydrogen and oxygen,
2. electrolysis of brine (sodium chloride) solution which yields hydrogen, chlorine, and sodium hydroxide solution, and
3. catalytic decomposition of saturated hydrocarbons.

Chemical Properties

Hydrogen, although relatively inactive at ambient temperatures, reacts with almost all the other elements at high temperatures. The reaction between hydrogen and oxygen at high temperatures is usually very violent. Hydrogen will reduce metallic oxides at elevated temperatures.

Thermodynamic and Detailed Physical Data

Molecular Structure

The homopolar hydrogen molecule has $D_{\infty h}$ symmetry, a symmetry number of two, and an internuclear H-H distance of 0.741 7 Å (0.741 7 × 10^{-10} m).

Infrared Spectrum

The hydrogen molecule is not infrared active, but it is Raman active.

Vapor Pressure (2)

The vapor pressures of normal H_2 (25% para) and 20.4 °K equilibrium H_2 (99.79% para) have been calculated from the Antoine vapor pressure equation:

$$\log_{10} p = A - \frac{B}{C + t} \quad \text{or} \quad t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 5.824 38, 67.507 8, and 275.700, respectively, for normal H_2, and 5.814 64, 66.794 5, and 275.650, respectively, for 20.4 °K equilibrium H_2.

Vapor pressure values calculated up to 1 500 mmHg as well as some other reported values are shown below.

Temperature, °K		Vapor Pressure		
Normal H_2	20.4 °K Equilibrium H_2	kPa	bar	mmHg
13.438	13.360	5.333	0.053	40
14.134	14.050	7.999	0.080	60
14.666	14.576	10.665	0.107	80
15.102	15.010	13.331	0.133	100
16.610	16.510	26.664	0.267	200
17.618	17.513	39.996	0.400	300
18.400	18.293	53.328	0.533	400
19.050	18.938	66.661	0.667	500
19.611	19.497	79.993	0.800	600
20.109	19.993	93.325	0.933	700
20.384	20.267	101.325	1.013	760
20.559	20.441	106.658	1.067	800
20.971	20.851	119.990	1.200	900
21.352	21.231	133.321	1.333	1 000
22.041	21.918	159.986	1.600	1 200
22.940	22.810	199.983	2.000	1 500
23.537	23.349	230.900	2.309	1 732
24.929	24.777	315.800	3.158	2 369
26.323	26.089	419.700	4.197	3 148
27.072	26.904	484.400	4.844	3 633
28.301	28.126	606.600	6.066	4 540
30.601	30.489	891.000	8.910	6 683
32.276	32.135	1 145.000	11.45	8 588

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/kg	
	Normal H_2	Para H_2
18	457.800	452.200
21	447.600	441.000
23	433.500	426.700

Thermodynamic Data

For the thermodynamic properties of superheated hydrogen, see Tables 1 and 2, respectively.

Thermodynamic Properties of Normal Hydrogen As Ideal Gas @ 25 °C (3)

Heat Capacity, C_p^o	28.836 J/(mol·°K)
Entropy, S^o	130.574 J/(mol·°K)
Free Energy Function, $(F_{298}^o - H_{298}^o/298)$	−130.574 J/(mol·°K)
Enthalpy Difference, $H_{298}^o - H_0^o$	8.468 kJ/mol
Enthalpy of Formation, ΔH_f^o	0.000 kJ/mol
Free Energy of Formation, ΔF_f^o	0.000 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of hydrogen, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, 1975, Matheson, East Rutherford, New Jersey.

[2] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds*, Volume 1, *1968*, Thermodynamic Research Center, Texas A & M University, College Station, Texas.

[3] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[4] J. Hilsenrath, *et al.*, *Tables of Thermal Properties of Gases*, Natl. Bur. Stand. Circular 564, *1955*, pp. 254–296, U. S. Government Printing Office, Washington, D. C.

Table 1. THERMODYNAMIC PROPERTIES OF SUPERHEATED NORMAL HYDROGEN (4)

H, ENTHALPY, KJ/KG; S, ENTROPY, KJ/(KG. °K); V, SPECIFIC VOLUME, CM^3/MOL

Pressure kPa	Pressure bar	atm		Temperature, °K 60	100	150	200	250	300	350	400	450	500	550	600
1.013	0.01	0.01	H	1 146.285	1 575.058	2 170.900	2 826.001	3 516.814	4 226.553	4 945.304	5 667.999	6 392.383	7 177.669	7 843.744	8 570.607
			S	64.148	69.609	74.422	78.187	81.264	83.850	86.068	87.998	89.702	91.323	92.618	93.884
			V	492.340	820.566	1 230.852	1 641.194	2 051.455	2 463.054	2 872.143	3 282.372	3 692.551	4 102.539	4 512.789	4 922.863
10.133	0.101	0.1	H	1 145.947	1 574.945	2 170.900	2 826.001	3 516.701	4 226.553	4 945.304	5 667.999	6 392.383	7 117.782	7 843.744	8 570.719
			S	54.650	60.111	64.923	68.689	71.766	74.356	76.570	78.500	80.208	81.734	83.124	84.386
			V	49.209	82.057	123.099	164.131	205.164	246.197	287.214	328.237	369.255	410.254	451.279	492.286
101.325	1.013	1.0	H	1 142.567	1 573.593	2 170.450	2 825.888	3 517.039	4 227.003	4 945.755	5 668.562	6 393.059	7 118.458	7 844.420	8 571.395
			S	45.111	50.600	55.421	59.191	62.267	64.857	67.072	69.002	70.710	72.236	73.626	74.888
			V	4.901	8.204	12.316	16.423	20.526	24.631	28.732	32.838	36.938	41.048	45.146	49.250
405.300	4.053	4.0	H												
			S	1 209.0	2 049.8	3 084.7	4 114.6	5 141.8	6 169.2	7 194.4	8 222.2	9 246.2	10 274	11 300	12 323
			V												
709.275	7.093	7.0	H												
			S	681.6	1 170.7	1 765.6	2 355.7	2 943.4	3 531.5	4 117.6	4 705.0	5 291.0	5 877.7	6 464.1	7 049.7
			V												
1 013.250	10.1	10.0	H	1 107.756	1 560.525	2 166.056	2 825.776	3 519.405	4 230.946	4 950.825	5 674.308	6 399.368	7 125.105	7 851.517	8 578.493
			S	35.200	40.982	45.874	49.668	52.757	55.351	57.574	59.504	61.212	62.742	64.127	65.394
			V	470.9	819.2	1 238.0	1 652.3	2 064.7	2 476.1	2 887.3	3 297.8	3 709.0	4 119.1	4 529.2	4 940.2
4 053.000	40.5	40.0	H												
			S	107.8	205.7	315.7	421.9	526.4	630.1	733.3	836.4	939.4	1 042.1	1 144.7	1 247.6
			V												
7 092.750	70.9	70.0	H												
			S	61.2	119.8	184.7	246.5	306.8	366.4	425.8	484.5	543.7	602.5	661.2	720.0
			V												
10 132.500	101.3	100.0	H	880.752	1 471.188	2 143.637	2 836.478	3 550.160	4 274.319	5 002.985	5 732.777	6 462.343	7 191.910	7 920.914	8 650.255
			S	22.918	30.519	35.967	39.955	43.135	45.779	48.027	49.973	51.693	53.227	54.621	55.891
			V	46.3	86.7	132.9	176.6	219.1	261.1	302.7	344.2	385.4	426.7	467.8	508.9

Table 2. COMPRESSIBILITY FACTORS FOR NORMAL HYDROGEN GAS (Z = PV/RT) (4)

Temperature, °K	Pressure, kPa 101.325	405.300	709.275	1 013.250	4 053.000	7 092.750	10 132.500
60	0.995 5	0.982 2	0.969 1	0.956 4	0.875 7	0.870 0	0.939 5
100	0.999 8	0.999 2	0.998 7	0.998 3	1.002 9	1.022 2	1.056 0
150	1.000 6	1.002 4	1.004 1	1.005 8	1.026 0	1.050 7	1.079.6
200	1.000 7	1.002 8	1.004 8	1.006 8	1.028.3	1.051 3	1.076 0
250	1.000 6	1.002 5	1.004 4	1.006 5	1.026.4	1.046 9	1.068 2
300	1.000 6	1.002 4	1.004 2	1.005 9	1.023 8	1.042 0	1.060 7
350	1.000 5	1.002 0	1.003 6	1.005 3	1.021 3	1.037 6	1.054 1
400	1.000 5	1.002 0	1.003 4	1.004 8	1.019 3	1.033 9	1.048 6
450	1.000 4	1.001 6	1.003 0	1.004 4	1.017 6	1.030 7	1.043 9
500	1.000 4	1.001 6	1.002 8	1.004 0	1.016 0	1.028.0	1.040 0
550	1.000 4	1.001 5	1.002 6	1.003 6	1.014 5	1.025 5	1.036 6
600	1.000 3	1.001 2	1.002 3	1.003 4	1 013 6	1.023 7	1.033 7

HYDROGEN BROMIDE

(Synonym: Anhydrous Hydrobromic Acid)
(Formula: HBr)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.080 912 kg
One Mole of HBr	0.080 912 kg
Specific Volume @ 21.1 °C, 101.325 kPa	299.6 dm^3/kg; 4.8 ft^3/lb
Vapor Pressure @ 21.1 °C	2 310 kPa; 23.1 bar; 334.7 psia; 22.8 atm
Boiling Point @ 101.325 kPa	206.43 °K; −66.7 °C; −88.1 °F
Triple Point	186.29 °K; −86.9 °C; −124.4 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	3.330 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	2.812
Density, Liquid @ −67.1 °C	2.717 kg/l
Critical Temperature	362.95 °K; 89.8 °C; 193.6 °F
Critical Pressure	8 510 kPa; 85.1 bar; 1 234.5 psia; 84.0 atm
Critical Volume	1.360 dm^3/kg
Critical Density	0.735 kg/dm^3
Critical Compressibility Factor	0.310
Latent Heat of Fusion @ −86.9 °C	2.406 kJ/mol; 29.74 kJ/kg; 0.575 kcal/mol
Dipole Moment	2.6×10^{-30} C·m; 0.78 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	29.791 J/(mol·°K)
@ Constant Volume	20.980 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.42
Molar Specific Heat, Liquid @ 35 °C	337.654 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.017 5 mPa·s; 0.017 5 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 26.7 °C	0.008 64 W/(m·°K): 20.66×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −67.1 °C	27.07 mN/m; 27.07 dyn/cm
Solubility In Water @ 101.325 kPa @ 25 °C	0.193 0 kg HBr/0.1 kg water
Dielectric Constant	
Gas @ 0 °C, 101.325 kPa	1.003 13
Liquid @ −85 °C	7.00
Refractive Index, Gas, n_D @ 25 °C	1.000 559 1

Description

Hydrogen bromide is a colorless, toxic and corrosive gas at atmospheric pressure and room temperature. It is severely irritating to the upper respiratory tract and corrosive to the eyes, skin, and mucous membranes. It is much heavier than air, and fumes in moist air. Hydrogen bromide is shipped in cylinders as a liquefied gas under its own vapor pressure of 2 210 kPa (320 psig) at 21.1 °C. Liquid hydrogen bromide has a yellowish color.

Specifications

Hydrogen bromide has a minimum purity of 99.8%.

Uses

Hydrogen bromide is used both as a reagent and a catalyst in a variety of organic reactions. It is also used for the preparation of numerous inorganic bromides.

Effects in Man (2) (3)

Inhalation of hydrogen bromide causes irritation of the upper respiratory tract, and a concentration of about 35 ppm causes irritation of the throat after short exposure. More severe exposures result in pulmonary edema, and often in laryngeal spasm.

Skin contact with the vapor or liquid causes severe tissue irritation and necrosis.

The vapors of hydrogen bromide are severely irritating to the mucous membranes of the eyes and nose.

Toxicity (4)

Concentrations of 1 300–2 000 ppm by volume in air are lethal to humans on brief exposures (up to a few minutes). Concentrations in the range of 1 000–1 300 ppm by volume in air are dangerous if breathed 30–60 minutes. The maximum concentration tolerated for exposure of 60 minutes is in the range of 50–100 ppm and the maximum tolerated for several hours of exposure is 10–50 ppm.

Hydrogen bromide is readily detectable in air by its sharp, penetrating odor.

The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 3 ppm (10 mg/m^3) for hydrogen bromide.

First Aid Treatment (2)

The following suggested treatment should be administered at once.

Inhalation

Inhalation of moderate amounts of the hydrogen bromide vapors causes choking and coughing. Exposed persons should leave the contaminated areas at once and breathe fresh air or oxygen. Severe exposure causes breathing to become labored or even stop. In such cases, the victim must be removed to an uncontaminated area and given artificial respiration (if breathing has stopped) or oxygen (if breathing is labored). The patient should be kept comfortably warm, but not hot, and a physician should be called at once. Observe for signs of pulmonary edema. If lungs are affected give antibiotics prophylactically. Rest is important.

Skin Contact

All areas of skin contacted by the hydrogen bromide should be washed off at once with running water, preferably under a drenching shower. The use of chemical neutralizers for this purpose is not recommended. Contaminated clothing must be removed at once. On severe exposure, shock symptoms such as rapid pulse, sweating, and collapse may appear and, in such cases, the victim should be kept warm and made to lie down until a physician arrives. The use of oils or ointments, unless prescribed by a physician, is not recommended.

Contact With Eyes

Any contact of the hydrogen bromide vapors with the eyes should be regarded as serious. Severe irritation of the eyes and eyelids may occur if the eyes are not washed out promptly, and prolonged contact may result in impairment or loss of vision.

If the eyes are affected, they should be irrigated without delay with copious quantities of running water, preferably using an eyewash fountain. The eyelids should be spread apart with the fingers to ensure thorough rinsing. Washing should continue for at least 15 minutes. A physician, preferably an eye specialist, should be called without delay. If the physician is not available, rinsing in running water should be continued for a second period of 15 minutes. After the first period of irrigation is completed, 2 or 3 drops of pontocaine (0.5% aqueous solution) may be instilled into the eye as a first aid measure.

Nose

If the mucous membranes of the nose are irritated, rinse with water for at least 15 minutes.

Precautions in Handling and Storage

(a) Workers who handle hydrogen bromide should wear protective clothing such as rubber or plastic aprons, rubber gloves, and suitable gas-tight chemical safety goggles. Woolen outside clothing or other acid resistant fabrics are recommended for workers handling hydrogen bromide.

(b) Instant-acting safety-showers should be available in the event of an emergency.

(c) Special eye-washing fountains or similar equipment should be available for eye irrigation.

(d) Proper respiratory equipment must be provided and personnel wearing such equipment must be carefully instructed in its operation and limitations.

(e) Precautions should always be taken to prevent suckback of foreign materials into the cylinder by using a check valve, vacuum break, or trap, since such a suckback may cause the development of dangerous pressures within the cylinder. The cylinder valve should be closed after each use.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Large leaks of hydrogen bromide will be evident by the formation of dense white fumes on contact with the atmosphere. Small leaks of hydrogen bromide may be detected by holding an open bottle of concentrated ammonium hydroxide solution near the site of the suspected leak (formation of dense white fumes). Wet blue litmus paper will turn pink when exposed to a hydrogen bromide leak.

Cylinder valve leaks can usually be corrected by tightening the valve packing nut (turn clockwise as viewed from above). If valve leaks persist or leaks appear at any portion of the cylinder, advise the supplier immediately.

Disposal of Leaking Cylinders

Leaking cylinders which cannot be corrected normally may be disposed of according to the procedure described in Appendix II-D.

Materials of Construction

Hydrogen bromide is essentially inert to metals and does not attack the commonly used structural metals under normal conditions of use (room temperature and atmospheric pressure). In the presence of moisture, however, hydrogen bromide will corrode most metals other than silver, platinum, and tantalum. When used at higher pressures, it is necessary to use extra heavy black iron pipe throughout. No galvanized pipe or brass or bronze fittings should be used as these will corrode. High pressure steel, monel or aluminum-iron-bronze valves

should be used throughout. Users of hydrogen bromide are warned to always shut off their hydrogen bromide lines from the use end, backward to the cylinders.

Cylinder and Valve Description

Anhydrous hydrogen bromide is shipped in DOT approved, high pressure steel cylinders. The assigned standard cylinder valve outlet and connection for hydrogen bromide and the one used by Matheson is Compressed Gas Association (CGA) No. 330. This valve outlet has a thread size of 0.825 inch diameter, having left-hand external threads, with a flat seat and used with a washer to seal. (See Figure 1 for an illustration of this valve outlet and its mating connection). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet.

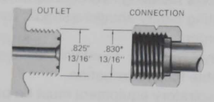


Fig. 1. CONNECTION 330 .825"-14 LH EXT. used with Flat Seat and Washer

Safety Devices

Cylinders of hydrogen bromide have safety devices consisting of platinum-plated frangible discs backed up with fusible metal plugs, melting about 73.9 °C (165 °F). The safety device is usually an integral part of the cylinder valve. Cylinders over 30 inches long, exclusive of the neck, require this device in both ends of the cylinder.

Recommended Controls

Automatic Pressure Regulators

Automatic regulators Models B15-330 and B16-330, having delivery pressure ranges of 28–345 kPa (4–50 psig) and 345–4 480 kPa (50–650 psig), respectively, are recommended for use with hydrogen bromide. These regulators have nickel coated brass bodies, with internal parts of monel. The diaphragms are chemically deposited pure nickel on nickel-silver alloy. Kel-F and Teflon are used for critical sealing and seating surfaces. The needle valve on the outlet end is monel. A monel check valve is recommended for use with these regulators to prevent suckback of foreign materials into the regulators.

Manual Controls

For manual flow control, needle valve Model 55-330 is supplied by Matheson for direct attachment to the cylinder valve outlet. This needle valve is of monel bar stock and may be equipped with a variety of outlets (hose connection, 1/4" tube fitting, and 1/4" NPT male or female outlets). It should be used only where manual flow control is needed and should not be used as a pressure control, since it will not prevent pressure from building up if a system becomes clogged, or if the system itself is closed. Models 60L and 33M needle valves are available for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory monel flowmeter units with 150 mm tubes and floats are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 should be used where accurate readings are required. Monel transducers must be used. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8260 of monel is designed to control the flow of gas regardless of pressure or temperature changes. This mass flow controller consists of a transducer, control valve, blind controller/power supply, potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Hydrogen bromide is classified by the DOT as a nonflammable gas and is shipped under "Green Label".

Chemical Preparation

1. Hydrogen bromide can be prepared by direct combination of hydrogen and bromine over platinized silica gel at 350–375 °C.
2. Hydrogen bromide is obtained as a by-product during the bromination of organic compounds.
3. It may be obtained by the bromination of tetrahydronaphthalene.
4. It may be obtained by heating an anhydrous methyl bromide with a strong nonoxidizing acid such as phosphoric acid.
5. It may be obtained by hydrolysis of a nonmetal bromide such as phosphorous tribromide.
6. It may be obtained by reduction of a noble-metal bromide such as silver bromide with hydrogen.
7. It may be obtained by the reaction of bromine with a covalent hydride such as hydrogen sulfide.

Chemical Properties

Hydrogen bromide adds to olefins and acetylenes. It is used in the laboratory both as a reagent and a catalyst in a variety of organic reactions. Hydrogen bromide is thermally stable. It is extremely soluble in water, forming a strong acid, and quite soluble in nonpolar solvents such as benzene. It is resistant to oxidation.

Thermodynamic and Detailed Physical Data

Molecular Structure (1)

The hydrogen bromide molecule is linear and has $C_{\infty v}$ symmetry and a symmetry number of one. The H—Br bond distance is 1.414×10^{-10} m 1.414 Å.

Matheson

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous hydrogen bromide.

Vapor Pressure

Vapor pressures up to 199.975 kPa (1 500 mmHg) conform to the following Antoine vapor pressure equation (2):

$$\log_{10} p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.283 70, 539.62, and 225.30, respectively. The following vapor pressure values have been calculated by this equation.

Temperature,	Vapor Pressure		
°K	kPa	bar	mmHg
183.35	26.659	0.267	200
189.61	39.993	0.400	300
194.42	53.327	0.533	400
198.38	66.652	0.667	500
201.78	79.986	0.800	600
204.78	93.320	0.933	700
206.43	101.325	1.013	760
207.47	106.655	1.067	800
209.95	119.989	1.200	900
212.15	133.313	1.333	1 000
216.25	159.982	1.600	1 200
221.45	199.975	2.000	1 500

Vapor pressures from 101.325 kPa (1 atm) up to the critical point are shown below (4).

Temperature, °K	Vapor Pressure		
	kPa	bar	atm
206.65	101.3	1.013	1
221.65	202.7	2.027	2
244.05	506.6	5.066	5
264.75	1 013	10.13	10
289.95	2 026	20.26	20
307.05	3 040	30.40	30
321.25	4 053	40.53	40
333.15	5 066	50.66	50
343.75	6 080	60.80	60
363.15 (C.T.)	8 552	85.52	84.4 (C.P.)

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/kg
200.00	221.1
206.43	217.7
210.00	215.8

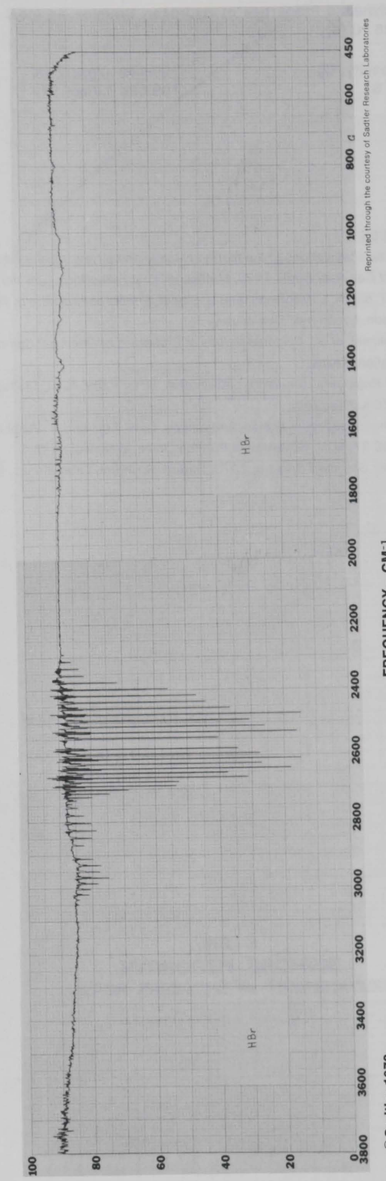


Fig. 2. Infrared spectrum of gaseous hydrogen bromide over the frequency region 3800 cm^{-1} to 450 cm^{-1}; 10 cm path length cell, with KBr optics; cell pressure (complete scan) 32–13 kPa (320 mmHg) (6).

Matheson

HYDROGEN BROMIDE

Thermodynamic Properties of Hydrogen Bromide As Ideal Gas @ 25 °C (5)			
		Free Energy Function, $(F^{\circ}_{298} - H^{\circ}_{298})/298$	−198.594 J/(mol·°K)
		Enthalpy Difference, $H^{\circ}_{298} - H^{\circ}_{0}$	8.648 kJ/mol
Heat Capacity, C°_{p}	29.142 J/(mol·°K)	Enthalpy of Formation, ΔH°_{f}	−36.443 kJ/mol
Entropy, S°	198.594 J/(mol·°K)	Free Energy of Formation, ΔF°_{f}	−53.492 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of hydrogen bromide, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, and A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 87–91, Matheson, Lyndhurst, New Jersey.

[3] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds, 1968*, Thermodynamic Research Center, Texas A & M University, College Station, Texas.

[4] *Chemical Engineers' Handbook*, 4th edition, R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, editors, *1963*, p. 3–43, McGraw-Hill Book Co., Inc., New York, New York.

[5] *JANAF Thermochemical Tables*, 2nd edition, D. R. Stull and H. Prophet, project directors, *1971*, *Natl. Stand. Ref. Data Ser.*, Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[6] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

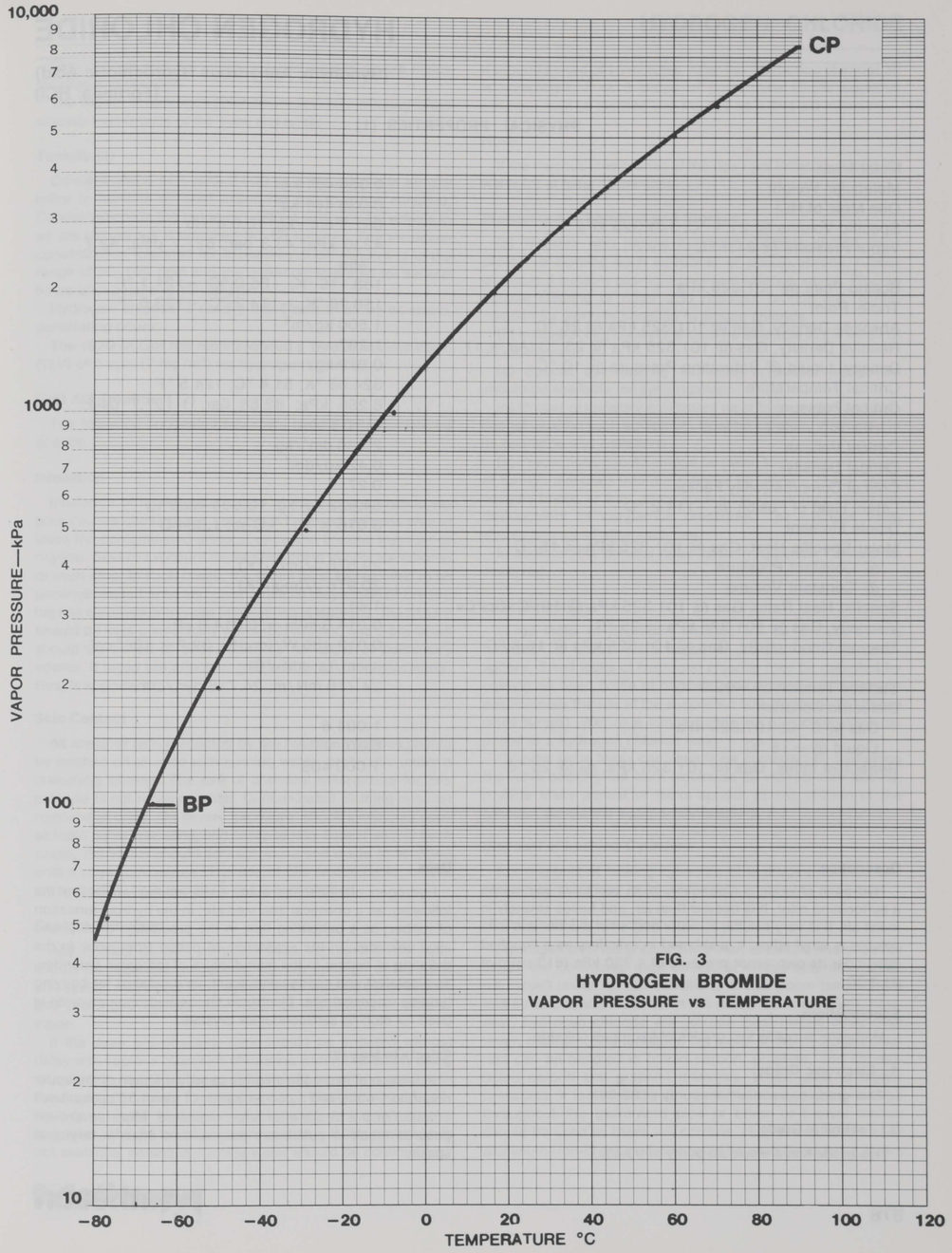


FIG. 3
HYDROGEN BROMIDE
VAPOR PRESSURE vs TEMPERATURE

HYDROGEN CHLORIDE

(Synonym: Anhydrous Hydrochloric Acid)
(Formula: HCl)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.036 461 kg
One Mole of HCl	0.036 461 kg
Specific Volume @ 21.1 °C, 101.325 kPa	661.7 dm^3/kg; 10.6 ft^3/lb
Vapor Pressure @ 21.1 °C	4330 kPa; 43.3 bar; 627.7 psia; 42.7 atm
Boiling Point @ 101.325 kPa	188.116 °K; −85.0 °C; −121.1 °F
Triple Point	158.96 °K; −114.2 °C; −173.5 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	1.500 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.267
Density, Liquid @ Saturation Pressure @ 10 °C	0.879 kg/l
Critical Temperature	324.55 °K; 51.4 °C; 124.5 °F
Critical Pressure	8 258 kPa; 82.58 bar; 1 197.7 psia; 81.5 atm
Critical Volume	2.386 dm^3/kg
Critical Density	0.42 kg/dm^3
Critical Compressibility Factor	0.27
Latent Heat of Fusion @ −114.2 °C	54.622 kJ/kg; 13.055 kcal/kg
Dipole Moment	3.616×10^{-30} C·m; 1.084 D
Molar Specific Heat, Gas @ 101.325 kPa @ 15 °C	
@ Constant Pressure	29.576 J/(mol·°K)
@ Constant Volume	20.976 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 15 °C, Cp/Cv	1.41
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.014 8 mPa·s; 0.014 8 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 15.6 °C	0.013 485 W/(m·°K); 32.2×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −92.9 °C	24.718 mN/m; 24.718 dyn/cm
Dielectric Constant	
Gas @ 0 °C, 101.325 kPa	1.004 6
Liquid @ −15 °C	6.35
Refractive Index, Gas @ 101.325 kPa, n_D @ 25 °C	1.000 408

Description

Hydrogen chloride is a pungent, toxic, corrosive gas having a suffocating odor. It is heavier than air, and fumes strongly in moist air. It is very soluble in water and ethyl alcohol and also soluble in ethyl ether. It is shipped in cylinders as a liquefied gas under its own vapor pressure of 4 230 kPa (613 psig) at 21.1 °C.

Specifications

Matheson supplies two grades of hydrogen chloride.

1. Electronic Grade

This grade has a minimum purity of 99.99%.

2. Technical Grade

This grade has a minimum purity of 99.0%.

Uses

Hydrogen chloride has many uses among which are the following: as a chemical intermediate; in the hydrochlorination of rubber; as a babbitting flux; in the production of vinyl and alkyl chlorides; in the separation of cotton from wool; in the delinting of cotton; in the manufacture of inorganic chlorides; as a catalyst and condensing agent; as a catalyst for bodying (adding viscosity) oils. Electronic Grade hydrogen chloride is used for etching semiconductor crystals.

Effects in Man (2)

Inhalation of hydrogen chloride causes irritation of the upper respiratory tract, and a concentration of about 35 ppm causes irritation of the throat after short exposure. More severe exposures result in pulmonary edema, and often in laryngeal spasm.

Skin contact with the vapor or liquid causes severe tissue irritation and necrosis.

The vapors of hydrogen chloride are severely irritating to the mucous membranes of the eyes and nose.

Toxicity (2)

Concentrations of 1 300–2 000 ppm by volume in air are lethal to humans on brief exposures (up to a few minutes). Concentrations in the range of 1 000–1 300 ppm by volume in air are dangerous if breathed 30–60 minutes. The maximum concentration tolerated for exposures of 60 minutes is in the range of 50–100 ppm and the maximum tolerated for several hours of exposure is 10–50 ppm.

Hydrogen chloride is readily detectable in air by its sharp, penetrating odors.

The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 5 ppm (7 mg/m^3) for hydrogen chloride.

First Aid Treatment (2)

The following suggested treatment should be administered at once.

Inhalation

Inhalation of moderate amounts of the hydrogen halide vapors causes choking and coughing. Exposed persons should leave the contaminated areas at once and breathe fresh air or oxygen. Severe exposure causes breathing to become labored or even stop. In such cases, the victim must be removed to an uncontaminated area and given artificial respiration (if breathing has stopped) or oxygen (if breathing is labored). The patient should be kept comfortably warm, but not hot, and a physician should be called at once. Observe for signs of pulmonary edema. If lungs are affected, give antibiotics prophylactically. Rest is important.

Skin Contact

All areas of skin contacted by the hydrogen halides should be washed off at once with running water, preferably under a drenching shower. The use of chemical neutralizers for this purpose is not recommended. Contaminated clothing must be removed at once. On severe exposure, shock symptoms such as rapid pulse, sweating, and collapse may appear and, in such cases, the victim should be kept warm and made to lie down until a physician arrives. The use of oils or ointments, unless prescribed by a physician, is not recommended.

Contact with Eyes

Any contact of the hydrogen halide vapors with the eyes should be regarded as serious. Severe irritation of the eyes and eyelids may occur if the eyes are not washed out promptly, and prolonged contact may result in impairment or loss of vision.

If the eyes are affected, they should be irrigated without delay with copious quantities of running water, preferably using an eyewash fountain. The eyelids should be spread apart with the fingers to ensure thorough rinsing. Washing should continue for at least 15 minutes. A physician, preferably an eye specialist, should be called without delay. If the physician is not available, rinsing in running water should be continued for a second period of 15 minutes. After the first period of irrigation is completed, 2 or 3 drops of pontocaine (0.5% aqueous solution) may be instilled into the eye as a first-aid measure.

Nose

If the mucous membranes of the nose are irritated, rinse with water for at least 15 minutes.

Precautions in Handling and Storage

(a) Workers who handle hydrogen chloride should wear protective clothing such as rubber or plastic aprons, rubber gloves,and suitable gas-tight chemical safety goggles. Woolen outside clothing or other acid resistant fabrics are recommended for workers handling hydrogen chloride.

(b) Instant-acting showers should be available in the event of an emergency.

(c) Special eye-washing fountains or similar equipment should be available for eye irrigation.

(d) Proper respiratory equipment must be provided and personnel wearing such equipment must be carefully instructed in its operation and limitations.

(e) Precautions should always be taken to prevent suckback of foreign materials into the cylinder by using a check valve, vacuum break, or trap, since such a suckback may cause the development of dangerous pressures. The cylinder valve should be closed after each use.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Large leaks of hydrogen chloride will be evident by the formation of dense white fumes on contact with the atmosphere. Small leaks of hydrogen chloride may be detected by holding an open bottle of concentrated ammonium hydroxide solution near the site of the suspected leak (formation of dense white fumes). Wet blue litmus paper will turn pink when exposed to a hydrogen chloride leak.

Cylinder valve leaks can usually be corrected by tightening the valve packing nut (turn clockwise as viewed from above). If valve leaks persist or leaks appear at any portion of the cylinder, advise the supplier immediately.

Disposal of Leaking Cylinders

For disposal of leaking cylinders of hydrogen chloride see procedure described in Appendix II-D.

Materials of Construction

Hydrogen chloride is essentially inert to metals and does not attack the commonly used structural metals (stainless steel, mild steel) under normal conditions of use (room temperature and atmospheric pressure). In the presence of moisture, however, hydrogen chloride will corrode most metals other than silver, platinum, and tantalum, but moist or dry hydrogen chloride can be handled in baked carbon, graphite, and impregnated carbon and graphite materials. When used at higher pressures, it is necessary to use extra heavy black iron pipe throughout. No galvanized pipe or brass or bronze fittings should be used as these will corrode. High pressure monel or aluminum-iron-bronze valves should be used throughout. Users

of hydrogen chloride are warmed to always shut off their hydrogen chloride lines from the use end, backward to the cylinders.

For more detailed information on materials of construction see Reference 3.

Cylinder and Valve Description

Hydrogen chloride is shipped in DOT approved, high pressure steel cylinders. Matheson uses aluminum-iron-bronze alloy valves with Compressed Gas Association (CGA) standard cylinder valve outlet and connection No. 330 on all cylinders of hydrogen chloride. This cylinder valve outlet has a thread size of 0.825 inch diameter, with left-hand external threads, with a flat seat, using a washer to seal (see Figure 1). Lecture bottles have a special 5/16"-32 threads per inch, female outlet.

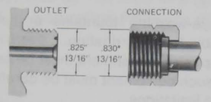


Fig. 1. CONNECTION 330 .825"-14 LH EXT. used with Flat Seat and Washer

Safety Devices

Cylinders of hydrogen chloride are equipped with safety devices which consist of platinum faced frangible discs (bursting at about 22 750 kPa (3 300 psig) at 71.1 °C (165 °F).

Recommended Controls

Automatic Pressure Regulators

The following single stage, corrosion resistant regulators are available for use with Electronic Grade hydrogen chloride:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
H15-330	28–345	0.28–3.45	4–50
H15A-330	28–345	0.28–3.45	4–50
H16-330	345–4 480	3.45–44.8	50–650
H16A-330	345–4 480	3.45–44.8	50–650

The following single stage, corrosion resistant regulators are available for use with Technical Grade hydrogen chloride:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
B15-330	28–345	0.28–3.45	4–50
B15A-330	28–345	0.28–3.45	4–50
B16-330	345–4 480	3.45–44.8	50–650
B16A-330	345–4 480	3.45–44.8	50–650

All the above regulators have chemically coated brass bodies, diaphragms of chemically deposited pure nickel on nickel-silver alloy, with internal parts of Monel. Kel-F and Teflon are used for critical sealing and seating surfaces. Model numbers containing an "A" have gauges for measuring tank and delivery pressure. The other models have single gauges indicating delivery pressure only. The needle valves on the outlets on the regulators used for Technical Grade hydrogen chloride are Monel. For the Electronic Grade hydrogen chloride, the Monel outlet valve has been replaced by an aluminum-silicon bronze diaphragm packless outlet valve with a 1/4" Monel Gyrolok tube fitting. The high purity regulators, H15 and H16 are capable of passing a helium leak test of 2×10^{-9} cm^3 per second.

A Monel check valve Model 402E is recommended for use with these regulators to prevent suckback of foreign materials into the regulators.

Manual Controls

For manual flow control, needle valve Model 55-330 is supplied by Matheson for direct attachment to the cylinder valve outlet. These needle valves are of monel bar stock and may be equipped with a variety of outlets such as a serrated hose end, 1/4" compression fitting, or 1/4" NPT male or female pipe. They should be used only where manual flow control is needed and should not be used as a pressure control since they will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. The Models 33M and 60L needle valves are available for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory Monel flowmeter units with 150 mm tubes and floats are recommended for use where definite flow rates must be know.

Monel electronic mass flowmeters, such as Matheson Series No. 8116, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8260 of Monel is designed to control the flow of gas regardless of pressure and temperature changes. This mass flow controller consists of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Hydrogen chloride is classified by the DOT as a nonflammable gas and is shipped under "Green Label".

Chemical Preparation

1. Commercially, hydrogen chloride is formed as a by-product in the manufacture of phenol in the initial step which involves the chlorination of benzene, and is available as a by-product from the chlorination of other hydrocarbons.
2. It is formed by direct reaction of chlorine and hydrogen.
3. It is formed by heating an anhydrous metal chloride with a strong nonvolatile acid.

Matheson

4. It is produced by hydrolysis of a nonmetal chloride such as phosphorous trichloride.
5. It is formed by reduction of a noble-metal chloride with hydrogen.

Chemical Properties

Hydrogen chloride is thermally stable, being 0.22% dissociated into hydrogen and chlorine at 1 800 °C. Hydrogen chloride is stable to oxidation except at elevated temperatures. Hydrogen chloride is extremely soluble in water. Its aqueous solution is a strong acid. Hydrogen chloride forms salts with amines, adds to olefins and acetylenes, replaces the hydroxyl group in the lower aliphatic alcohols (a process which may require the use of dehydrating agents depending on the alcohol used), and acts catalytically in numerous organic reactions.

Thermodynamic and Detailed Physical Data

Molecular Structure

The linear heteropolar HCl molecule has $C_{\infty v}$ symmetry, a symmetry number of one, and an H—Cl bond distance of 1.274 6 Å (1.274 6 × 10^{-10} m).

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous hydrogen chloride.

Vapor Pressure

The vapor pressure of liquid hydrogen chloride from 152.584 °K to 200.960 °K is expressed by the following Antoine vapor pressure equation (4):

$$\log_{10} p = A - \frac{B}{C + t} \quad \text{or} \quad t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 7.167 610, 744.490 6, and 258.704, respectively.

The following vapor pressure data have been calculated by this equation.

Temperature,	Vapor Pressure		
°K	kPa	mbar	mmHg
152.584	7.999	80.00	60
155.863	10.666	106.7	80
158.515	13.331	133.3	100
163.597	19.998	200.0	150
167.426	26.664	266.6	200
170.534	33.330	333.3	250
173.169	39.996	400.0	300
177.513	53.328	533.3	400
181.049	66.661	666.6	500
184.055	79.993	799.9	600
186.682	93.326	933.3	700
188.116	101.325	1 013.25	760
189.024	106.658	1 067	800
191.143	119.990	1 200	900
193.08	133.322	1 333	1 000
196.54	159.987	1 600	1 200
200.96	199.984	2 000	1 500

The vapor pressure of hydrogen chloride above 101.325 kPa (1 atm) is shown below (5).

Temperature,	Vapor Pressure		
°K	kPa	bar	atm
188.116 (B.P.)	101.325	1.013 25	1
201.75	202.650	2.03	2
222.65	506.625	5.07	5
241.45	1 013.250	10.1	10
264.35	2 026.500	20.3	20
279.05	3 039.750	30.4	30
290.95	4 053.000	40.5	40
301.05	5 066.250	50.7	50
309.35	6 078.500	60.8	60
324.55 (C.T.)	8 257.988	82.6	81.5 (C.P.)

See Figure 3 for vapor presure curve.

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/kg
173.15	462.435
188.116	442.945
198.15	437.851

Thermodynamic Properties of Hydrogen Chloride As Ideal Gas @ 25 °C

Heat Capacity, C_p°	29.137 J/(mol·°K)
Entropy, S°	186.795 J/(mol·°K)
Free-Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−186.795 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	8.640 kJ/mol
Enthalpy of Formation, ΔH_f°	−92.312 kJ/mol
Free Energy of Formation, ΔF_f°	−95.303 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of hydrogen chloride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

Matheson

[2] W. Braker, A. L. Mossman, and D.Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 87–91, Matheson, Lyndhurst, New Jersey.

[3] W. R. Kleckner and R. C. Sutter, in Kirk-Othmer's *Encyclopedia of Chemical Technology*, 2nd edition, *1966*, Volume II, pp. 323–327, John Wiley & Sons, Inc., New York, New York.

[4] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds*, *1968*, Volume I, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[5] *Chemical Engineers' Handbook*, 4th edition, R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, editors, *1963*, p. 3–43, McGraw-Hill Book Co., Inc., New York, New York.

[6] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[7] *The Sadtler Standard Spectra*, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

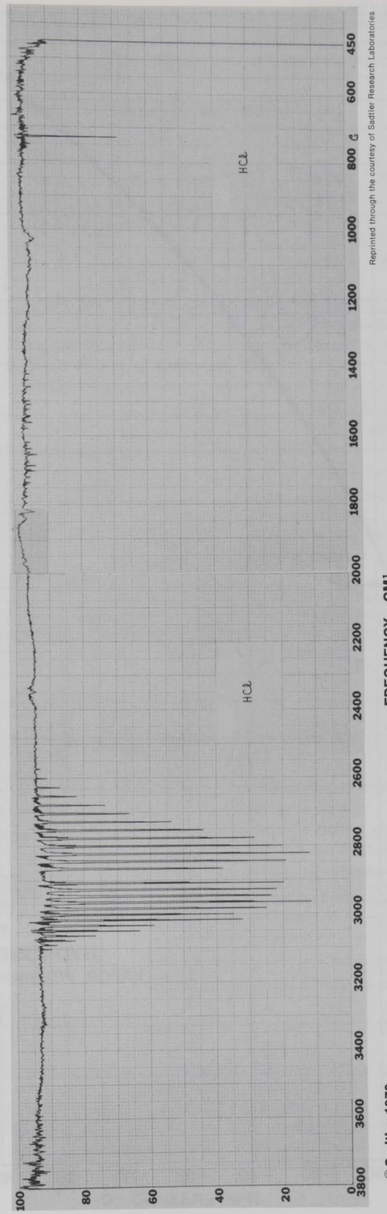


Fig. 2. Infrared spectrum of gaseous hydrogen chloride over the frequency region of 3 800 cm^{-1} to 450 cm^{-1}; 10 cm path length cell, with KBr windows; cell pressure (complete scan): 14.67 kPa (110 mmHg) (7).

Matheson

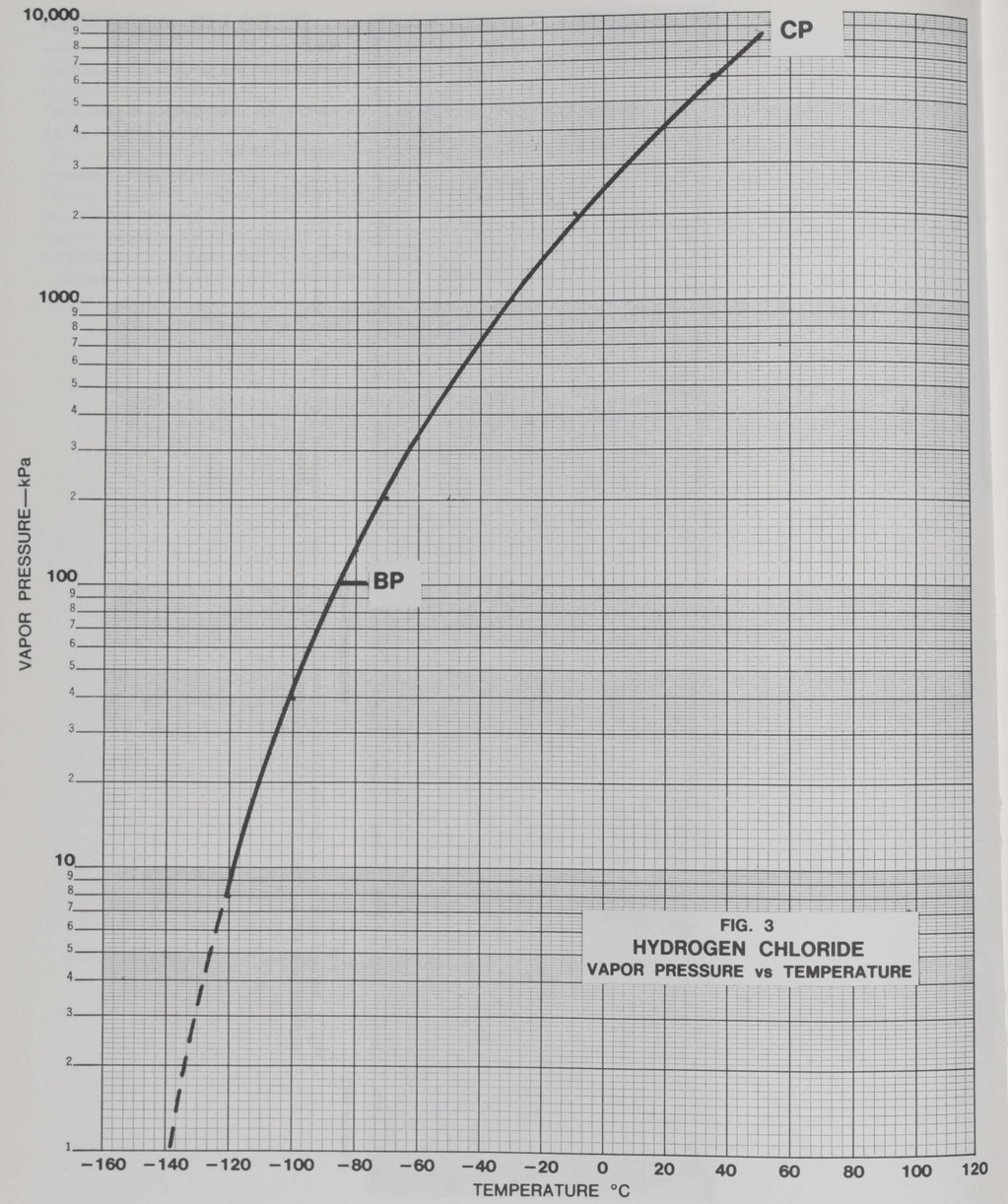


FIG. 3
HYDROGEN CHLORIDE
VAPOR PRESSURE vs TEMPERATURE

Matheson

HYDROGEN CYANIDE

(Synonyms: Hydrocyanic Acid; Prussic Acid; Formonitrile)
(Formula: HCN)

PHYSICAL PROPERTIES (1)

Molar Mass	0.027 026 kg
Molecular Weight	0.027 026 kg
One Mole of HCN	210 kPa; 2.1 bar; 30.24 psia; 2.06 atm
Vapor Pressure @ 46.3 °C	298.85 °K; 25.7 °C; 78.3 °F
Boiling Point @ 101.325 kPa	259.90 °K; −13.2 °C; 8.2 °F
Freezing Point	
Triple Point	259.833 °K; −13.3 °C; 8.0 °F
Temperature	18.63 kPa; 186.3 mbar; 139.7 mmHg
Pressure	1.099 2 kg/m^3
Absolute Density, Gas @ 101.325 kPa @ 31 °C	0.947
Relative Density, Gas @ 101.325 kPa @ 31 °C (Air = 1)	0.679 72 kg/l
Density, Liquid @ Saturation Pressure @ 25 °C	456.75 °K; 183.6 °C; 362.5 °F
Critical Temperature	5 390 kPa; 53.9 bar; 781.8 psia; 53.2 atm
Critical Pressure	5.143 dm^3/kg
Critical Volume	0.194 kg/dm^3
Critical Density	0.197
Critical Compressibility Factor	311.21 kJ/kg; 74.38 kcal/kg
Latent Heat of Fusion @ −13.2 °C	6–41% (by volume)
Flammability Limits In Air	
Molar Specific Heat, Gas @ 101.325 kPa @ 35 °C	39.024 J/(mol·°K)
@ Constant Pressure	29.789 J/(mol·°K)
@ Constant Volume	1.31
Specific Heat Ratio, Gas @ 101.325 kPa @ 35 °C, Cp/Cv	70.481 J/(mol·°K)
Molar Specific Heat, Liquid @ 4.0 °C	9.94×10^{-30} C·m; 2.98 D
Dipole Moment, Gas	0.002 9 mPa·s; 0.002 9 cP
Viscosity, Gas @ 101.325 kPa @ 50 °C	0.177 8 mPa·s; 0.177 8 cP
Viscosity, Liquid @ 25 °C	0.012 966 W/(m·°K); 31.0×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Gas @ 101.325 kPa @ 37.8 °C	18.33 mN/m; 18.33 dyn/cm
Surface Tension @ 20 °C	114.9
Dielectric Constant, Liquid @ 20 °C	3.3×10^{-6} 1/(Ω·cm)
Electrical Conductivity, Liquid @ 0 °C	811 °K; 538 °C; 1 000 °F
Autoignition Temperature	255.15 °K; −18 °C; −0.4 °F
Flash Point (closed cup)	1.261 4
Refractive, Index, n_D @ 20 °C	

Description

Hydrogen cyanide is a colorless, flammable liquid (at below 298.85 °K (78.26 °F)), with the characteristic odor of bitter almonds. Its vapor is highly toxic. It is shipped as a liquid in steel cylinders and has a vapor pressure of 78 kPa (11.3 psia) at 18.9 °C. It is stabilized with about 0.6% sulfuric acid or phosphoric acid.

Uses

The largest use (about 52%) is in the manufacture of acrylonitrile. About 18% of hydrogen cyanide production is used in the manufacture of methyl methacrylate. About 14% of the production is used to manufacture adiponitrile (for nylon). About 7% is used in the manufacture of sodium cyanide. The remainder is used to produce small amounts of ferrocyanides,

Matheson

acrylates, ethyl lactate, lactic acid, chelating agents, and pharmaceuticals.

Effects in Man (2)

Exposure to high concentrations of vapors (above around 100 ppm), or skin contact with liquid hydrogen cyanide, may be followed by instantaneous collapse and cessation of breathing. At much lower concentrations (about 18–36 ppm), the earliest symptoms may be simply those of dizziness, weakness, headache, confusion and occasionally nausea and vomiting. The respiratory rate and depth will usually be increased at the beginning and at later stages become slow and gasping. Blood pressure is usually normal, especially in mild or moderately severe cases, although the pulse rate is usually more rapid than normal. It is characteristic that the heart beat may continue for some time even after respiration has ceased.

Hydrogen cyanide has a characteristic odor, described variously as garlicky, oniony and that of oil of bitter almonds, which the trained individual can recognize at a concentration of 2–5 ppm by volume in air. There is wide individual variation in the minimum odor threshold.

The 1979 ACGIH has established a Threshold Limit Value (TLV) of 10 ppm (11 mg/m^3) for hydrogen cyanide.*

First Aid Treatment (2)

General

First aid must be administered *immediately*. A physician must be called at once and told the exact location of the victim and the nature of the accident.

Inhalation

Walk, carry or drag the victim to fresh air. Have him lie down. Place blankets over his body to maintain body heat.

(1) If the victim is conscious and breathing, watch him carefully for asphyxiation; if he lapses into unconsciousness, break an amyl nitrite pearl in a cloth and hold it close to the victim's nose for 15 seconds. (In this and in all subsequent administrations of amyl nitrite, the person giving first aid should keep the broken pearls away from his own mouth and nose; otherwise, he himself may inhale sufficient amyl nitrite to become dizzy, and be rendered incapable of giving proper first aid). Repeat this procedure only if necessary (when there is no response) and only a maximum of 5 times for 15 seconds at 15 second intervals, using a clean cloth and fresh pearl each time. This procedure alone may suffice for some of the milder cases provided the sources of absorption are also removed (e.g., residual hydrogen cyanide on the skin). In more serious cases, if there is no response to the amyl nitrite inhalations, it is necessary to produce methemoglobin in greater amounts by use of thiosulfate (see section on Suggested Medical Treatment below).

(2) If the victim is unconscious but breathing, the above described procedure of amyl nitrite inhalation is started immediately. Oxygen should then be administered.

(3) If the victim is not breathing, immediately start artificial respiration and continue until breathing starts. Then begin the amyl nitrite inhalations described above. Finally, administer oxygen.

In all cases, keep the victim quiet and warm until he has fully recovered.

Skin Contact

Immediately deluge the affected area with water (from an emergency shower, hose, etc.). Walk, carry, or drag the victim to fresh air. Remove wet clothing, shoes, and socks. Wash the skin thoroughly with copious amounts of water. Have the victim lie down, and place blankets under and over his body to maintain body heat.

If poisoning occurs as a result of skin contact, apply the first aid procedure appropriate to the effect produced (see sections above).

Suggested Medical Treatment

If there is no response to the amyl nitrite inhalations, it is necessary to inject intravenously 0.3 g of sodium nitrite (10 ml of a 3% solution at a rate of 2.5–5.0 ml/min), followed at once by 12.5 g of sodium thiosulfate intravenously (50 ml of a 25% solution injected at about the same rate as the sodium nitrite solution). The same needle and vein can be used for both injections. Watch the victim continuously for 24–48 hours. If symptoms recur or persist, repeat the sodium nitrite and sodium thiosulfate therapy at half the original doses.

First Aid and Medical Supplies

The following supplies should always be on hand in a convenient, safe location:

1. Two boxes (2 dozen) of amyl nitrite pearls.
2. Two ampules of sterile sodium nitrite solution (10 ml of a 3% solution in each).
3. Two ampules of sterile sodium thiosulfate solution (50 ml of a 25% solution in each).
4. Two 10 ml sterile syringes.
5. Two 50 ml sterile syringes.
6. Two sterile intravenous needles.
7. One tourniquet.
8. Twelve gauze pads.
9. One bottle of 70% alcohol.
10. One ampule file.

Precautions in Handling and Storage

1. Never work alone. Always have two people on the job.
2. All personnel must be able to recognize the symptoms of hydrogen cyanide poisoning and be able to administer first aid to victims.
3. All personnel must be trained to administer artificial respiration; if a resuscitator is available, personnel should be trained in its use.
4. Always check the nearest safety shower before starting a job involving handling of hydrogen cyanide. Do not start work unless the shower is in satisfactory working condition.
5. Provide adequate ventilation and avoid breathing hydrogen cyanide gas.
6. Have air masks readily available when working with hydrogen cyanide.
7. Wear a face shield when making or breaking connections on cylinders or operating valves in hydrogen cyanide lines.
8. In the event of release of hydrogen cyanide, hold your breath (do not inhale first), immediately don air mask, and leave the area until the severity of the break or release can be determined. Report this to supervisor at once.
9. Approach all hydrogen cyanide leaks from the up-wind direction.
10. Avoid contact of hydrogen cyanide with the skin. In case of contact, flush skin area immediately with large quantities of water.
11. Always wear rubber gloves when working on hydrogen cyanide cylinders or lines. If hydrogen cyanide is accidently spilled into the goves, remove gloves promptly and wash hand and gloves thoroughly with plenty of water.
12. Check all valves before and after withdrawing hydrogen cyanide from the cylinder.
13. Never trap liquid hydrogen cyanide between two valves.
14. Keep cylinder of hydrogen cyanide cool and away from open flames.
15. Make certain that hydrogen cyanide cylinders are adequately supported and grounded during storage and emptying.
16. Store cylinders in a vertical position. Do not drop cylinders or damage them by impact.
17. Cylinders must be returned to the supplier within 90 days of the filling date marked on the cylinders, regardless of whether or not the contents have been used. This is due to the possibility of hydrogen cyanide becoming unstable over time. If there is ever any indication that the hydrogen cyanide is becoming unstable, such as a darkening of the product or an increase in cylinder pressure, contact the supplier immediately for instructions.
18. Avoid addition of such alkaline chemicals as sodium hydroxide, ammonia, calcium hydroxide, and sodium carbonate to hydrogen cyanide since they promote polymerization and induce decomposition, which may cause an explosion. Also, avoid addition of large quantities of acid to hydrogen cyanide, for similar reasons.
19. Hydrogen cyanide is discharged from cylinders by pressure from uncontaminated nitrogen gas.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks in equipment and lines to contain hydrogen cyanide should be pretested with a dry, inert gas such as nitrogen.

There are numerous chemical methods for the detection and determination of hydrogen cyanide. These, including two of the more widely used detection tests, namely, the methyl orange-mercuric chloride test and the benzidine-copper acetate test, are described in literature by Jacobs.

The Matheson-Kitagawa Toxic Gas Detector System Model 8014K is available to measure high range (0.01–3.0%) and low range (2–100 ppm) concentrations of hydrogen cyanide in the atmosphere, using the Model 112SA and 112SB detector tubes, respectively. A constant color stain is produced which varies in length according to the concentration of the hydrogen cyanide being measured. The length of the stain, and hence, the concentration, is read directly from the tube.

Disposal of Hydrogen Cyanide

Hydrogen cyanide residues can be converted to sodium cyanide by addition to an excess of sodium hydroxide solution with agitation. Addition of sodium hypochlorite solution (household bleach) will destroy the cyanide by oxidation to cyanate.

Materials of Construction

Hydrogen cyanide may generally be handled in low-carbon steel equipment among others at ambient temperature. At high temperatures, stainless steel may be the material of choice.

Cylinder and Valve Description

Hydrogen cyanide is shipped in DOT approved, poison gas, steel cylinders. The CGA recommended standard connection for hydrogen cyanide is the No. 750 connection. However, because of widespread availability and use, most cylinders are equipped with brass valves with Compressed Gas Association (CGA) alternate standard valve outlet connection No. 660. The valve outlet has a thread size of 1.030″-14 RH Ext., with right-hand external threads. (See Figure 1 for an illustration of this valve outlet and its mating connection).

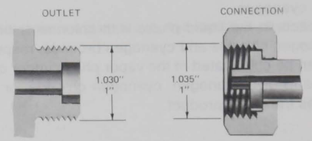


Fig. 1. CONNECTION 660 1.030″-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders of hydrogen cyanide are not equipped with safety devices. They should, therefore, be stored away from sources of heat to avoid dangerous hydrostatic pressures from developing within the cylinder.

Recommended Controls

Manual Controls

Manual needle valve Model 3712M2S fitted with a Model 2CF2 fitting and 12″ of ⅛″ tubing can be directly connected to the cylinder opening to permit withdrawal of liquid hydrogen cyanide under nitrogen pressure.

Shipping Regulations

Hydrogen cyanide is classified by the DOT as a "Class A" poison and is shipped with the required "Poison Gas Label".

Commercial Preparations

Hydrogen cyanide is manufactured by reacting methane (natural gas), ammonia and air over a platinum catalyst at

* 1979 Notice of intended change to 10 ppm (10 mg/m^3).

HYDROGEN CYANIDE

1 000–2 000 °C. Other methods include generation from sodium cyanide by a mineral acid; dehydration of formamide over catalysts, such as alumina, at 200–650 °C; reaction of nitric oxide and gasoline at 1 400 °C; reaction of hydrocarbons, ammonia and oxygen at 600–1 500 °C; reaction of nitrogen, hydrogen and carbon in an electric arc.

Chemical Properties

1. Hydrogen cyanide adds to alkynes in the presence of catalysts to give the corresponding alkenyl nitrile, e.g., liquid or vapor phase reaction of acetylene with HCN gives acrylonitrile, CH_2:CHCN, in high yield (up to 80–90%).
2. It is used in the Gattermann synthesis of aromatic aldehydes, by formylation of certain aromatic compounds, phenols, and phenolic ethers with HCN + HCl usually in the presence of $AlCl_3$ or $ZnCl_2$.
3. It is used in the Ritter reaction to prepare tertiaryalkyl amines, e.g., reaction of tertiary butyl alcohol or isobutylene with concentrated H_2SO_4 and HCN in acetic acid as solvent, followed by hydrolysis gives N-tert-butylformamide, $HCONHC(CH_3)_3$, which on further hydrolysis yields tertbutylamine, $(CH_3)_3CNH_2$.
4. It adds to aldehydes and ketones in the presence of basic catalysts to form cyanohydrins.
5. It can be oxidized by air at 300–650 °C. over silver or gold catalysts to give yields of up to 64% cyanic acid (HOCN) and 26% cyanogen.
6. It reacts in the liquid phase with chlorine or bromine to give cyanogen chloride and cyanogen bromide, respectively.
7. It can be chlorinated in the vapor phase under controlled conditions to give cyanogen, cyanogen chloride, or cyanuric chloride as the major product.

Thermodynamic and Detailed Physical Data

Molecular Structure (1)

The linear hydrogen cyanide molecule has $C_{\infty v}$ symmetry, a symmetry number of one, and H—C and C—N bond distances of 1.066 Å (1.066 × 10^{-10} m) and 1.153 Å (1.153 × 10^{-10} m), respectively.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous hydrogen cyanide.

Vapor Pressure

The vapor pressure up to 101.325 kPa (1 atm) is shown below (3).

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
259.89	18.624	186.2	139.7 (14)
261.39	20.238	202.4	151.8 (14)
265.133	24.224	242.2	181.70
268.067	27.884	278.8	209.15
272.054	33.568	335.7	251.78
276.271	40.545	405.5	304.11
285.070	59.040	590.4	442.84
289.979	72.051	720.5	540.43
295.235	87.823	878.2	658.73
298.851	101.346	1 013.5	760.16

Vapor pressures up to the critical point are shown below (15).

Temperature, °K	Vapor Pressure kPa	bar	atm
299.05	101.325	1.013 25	1
318.95	202.650	2.03	2
348.95	506.625	5.07	5
375.85	1 013.250	10.1	10
408.15	2 026.500	20.3	20
426.95	3 039.750	30.4	30
443.05	4 053.000	40.5	40
456.75 (C.T.)	5 390.490	53.9 (C.P.)	53.2 (6)

See Figure 3 for vapor pressure curve.

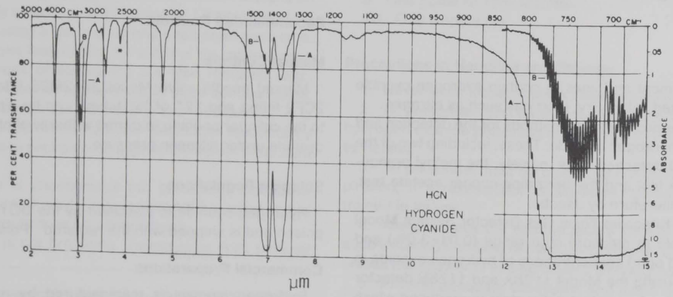


Fig. 2. Infrared spectrum of gaseous hydrogen cyanide, obtained with sodium chloride optics and 10 cm cell; curve A obtained at cell pressure 94.26 kPa (707 mmHg), curve B at 7.47 kPa (56 mmHg) (8).

Latent Heat of Vaporization, ΔHv

Temperature, °C	ΔHv, kJ/kg
0	988
25.7	933

Thermodynamic Properties of Hydrogen Cyanide As Ideal Gas @ 25 °C (7)

Heat Capacity, C_p^o	35.857 J/(mol·°K)
Entropy, S^o	201.719 J/(mol·°K)
Free Energy Function, $(F_{298}^o - H_{298}^o)/298$	−201.719 J/(mol·°K)
Enthalpy Difference, $H_{298}^o - H_0^o$	9.234 kJ/mol
Enthalpy of Formation, ΔH_f^o	135.143 kJ/mol
Free Energy of Formation, ΔF_f^o	124.708 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of hydrogen cyanide, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1970*, pp. 32–38, Matheson, Lyndhurst, New Jersey.

[3] R. A. Ruehrwein and W. F. Giauque, *J. Amer. Chem. Soc.* 61, 2626 (1939).

[4] J. Lange and J. Berga, *Monatsh.* 81, 921 (1950).

[5] *Chemical Engineers' Handbook*, 4th edition, R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, editors, *1963*, p. 3-45, McGraw-Hill Book Company, Inc., New York, New York.

[6] J. F. Mathews, *Chem. Rev.* 72, 96 (1972).

[7] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[8] R. H. Pierson, A. N. Fletcher, and E. St. Clair Gantz, *Anal. Chem.* 28, 1218 (1956).

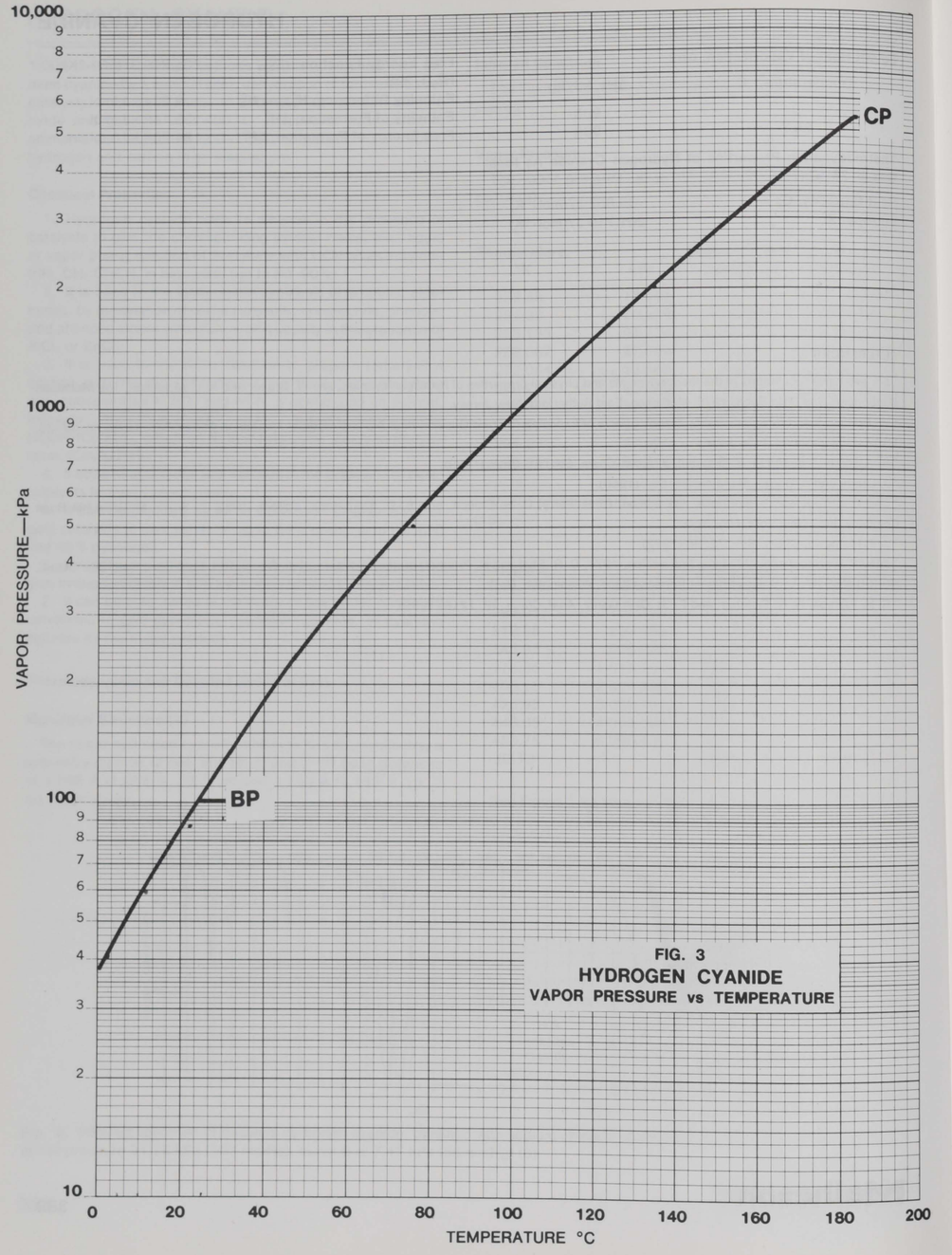


FIG. 3
HYDROGEN CYANIDE
VAPOR PRESSURE vs TEMPERATURE

HYDROGEN FLUORIDE

(Synonym: Anhydrous Hydrofluoric Acid)
(Formula: HF)

PHYSICAL PROPERTIES (1)

Molar Mass	
80 °C, 101.325 kPa	0.020 006 4 kg
One Mole of HF	0.020 006 4 kg
Molar Mass	
Molecular Weight	
Saturated Vapor @ 20 °C	74.88 (3.743 moles HF associated)
Saturated Vapor @ 100 °C	49.08 (2.453 moles HF associated)
Specific Volume @ 21.1 °C, 101.325 kPa	1 204.8 dm^3/kg; 19.3 ft^3/lb
Vapor Pressure @ 20 °C	103 kPa; 1.03 bar; 15.0 psia; 1.03 atm
Boiling Point @ 101.325 kPa	292.67 °K; 19.5 °C; 67.1 °F
Triple Point	189.78 °K; −83.4 °C; −118.1 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	2.201 kg/dm^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.858
Density, Liquid @ 19.5 °C	0.957 kg/l
Critical Temperature	461.15 °K; 188.0 °C; 370.4 °F
Critical Pressure	6 485 kPa; 64.85 bar; 940.5 psia; 64.0 atm
Critical Volume	69 cm^3/0.020 01 kg
Critical Density	0.290 kg/dm^3
Critical Compressibility Factor	0.12
Latent Heat of Fusion @ −83.4 °C	196.355 kJ/kg; 46.93 kcal/kg
Dipole Moment, Monomer	6.104×10^{-30} C·m; 1.83 D
Specific Heat, Gas @ 101.325 kPa @ 30 °C	
@ Constant Pressure	807.51 J/(0.020 01 kg·°K)
@ Constant Volume	47.698 J/(0.020 01 kg·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 30 °C, Cp/Cv	16.93
Specific Heat, Liquid @ 15.9 °C	50.585 J/(0.020 01 kg·°K)
Viscosity, Liquid @ 0 °C	0.256 mPa·s; 0.256 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 100.6 °C	0.025 47 W/(m·°K); 60.8×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 0 °C	10.1 mN/m; 10.1 dyn/cm
Dielectric Constant, Liquid @ 0 °C	83.6
Specific Conductivity @ 0 °C	$1.6 \times 10^{-6}\ \Omega^{-1}$/cm
Refractive Index, Gas @ 25 °C and 5 893 Å	1.157 4

Description

Hydrogen fluoride is a colorless, corrosive toxic liquid or gas, depending on the temperature. Because its boiling point 292.67 °K (19.5 °C) is often exceeded by the temperature at which it is transported or used, it is shipped in cylinders under its own vapor pressure of 2.1 kPa (0.3 psig) at 20 °C.

Hydrogen fluoride differs in many ways from the other hydrogen halides because of its greater ionic character and its tendency to associate through hydrogen bonding. Association characterizes the liquid state and continues into the vapor state. Dipole moment calculations and dielectric constant measurements of the vapor indicate the formation of more or less linear polymers as indicated by x-ray and electron diffraction measurements (2). However, the presence of cyclic polymers is also indicated. The degree of polymerization or molecular association is a controversial matter.

Specifications

Hydrogen fluoride as supplied by Matheson has a minimum purity of 99.9%.

Uses

Hydrogen fluoride is used to prepare fluorides, to manufacture fluorine, as a catalyst in isomerization, condensation,

dehydration, polymerization, and hydrolysis reactions, and as a fluorinating agent in organic and inorganic reactions. It is also used as an alkylation catalyst in the petroleum industry, for etching and polishing of glass, and in the manufacture of aluminum fluoride and synthetic cryolite.

Toxicity and Effects in Man (3)

The concentration that produces acute effects varies with the time of exposure; 50 ppm may be fatal if inhaled for 30–60 minutes. Less severe exposures cause irritation of the nose and eyes, smarting of the skin, some degree of conjuctival and respiratory irritation. More severe exposures can lead to severe irritation of the eyes and eyelids and to inflammation and congestion of the lungs and circulatory (cardiovascular) collapse. Skin contact with the liquor or vapor of any member of this group can cause severe burns.

Hydrogen fluoride is readily detectable in air by its sharp, irritating odor.

The 1979 ACGIH has established a Threshold Limit Value (TLV) of 3 ppm (2 mg/m^3) for hydrogen fluoride (as F).

First Aid Treatment (3)

Speed in removing the patient from the contaminated atmosphere or removing the vapor or liquid from the skin or eyes is essential. First aid must be started immediately in all cases of contact with the particular gas in any form. All affected persons should be referred to a physician, no matter how slight the injury, and the physician given a detailed account of the accident.

Inhalation

In minor exposures, remove the victim to an uncontaminated atmosphere and administer as quickly as possible 100% oxygen. It has been found helpful to expose even borderline cases to 100% oxygen at half hour intervals for 3–4 hours.

In severe exposures, the worker must be carried at once into an uncontaminated atmosphere. A physician should be called immediately and the administration of 100% oxygen should be started at once. The victim should receive oxygen under positive pressure (<4 cm) for half hour periods for at least 6 hours until breathing is easy and the color of the skin and mucous membranes is normal. He should be kept comfortably warm, but not hot. Under no circumstances should the patient be permitted to return home or to work following a severe exposure until examined and discharged by a physician who is aware of the nature of the exposure. Mild analgesics and sedatives, such as aspirin or sodium bromide, may be given if thought to be desirable by the physician, but medication is usually unnecessary when adequate oxygen has been administered immediately after exposure. Morphine and barbiturates should never be given because of their depressant effect on respiration. Cardiac and respiratory stimulants are not recommended.

Artificial respiration should not be given unless breathing has ceased.

Contact With Eyes

If the eyes have been contacted by hydrogen fluoride, they should be flushed with water for 15 minutes. This may have to be repeated several times. Ice compresses should be applied when not irritating. Pain can be relieved by 2 or 3 drops of 0.5% tetracaine (pontocaine). An ophthalmologist may be interested in a method of treatment for chemical burns of the eye described by R. S. McLaughlin in the American Journal of Ophthalmology 29, 1355 (1946).

Contact With Skin

Workers who have had skin contact with hydrogen fluoride should be subjected to a drenching shower of water. The clothing should be removed as rapidly as possible, even while the victim is in the shower, and medical assistance obtained immediately. It is essential that the affected area be washed with copious quantities of water for a sufficient period of time to remove all acid from the skin. The affected part should then be immersed in an ice-cold saturated solution of magnesium sulfate (Epsom salt), iced 70% alcohol, or an iced aqueous or alcoholic solution of Hyamine, a high molecular weight quaternary ammonium compound. The immersed part should be removed for 2–3 minutes every 10 minutes to relieve the discomfort. If the burn is in such an area that it is impractical to immerse the part, then iced alcohol, iced magnesium sulfate solution, or Hyamine solution should be applied in the form of saturated compresses, which should be changed at least every 2 minutes. This treatment should be continued for 1–4 hours depending on the extent of the burn. The area should then be covered with a generous quantity of paste freshly prepared from powdered U.S.P. magnesium oxide and U.S.P. glycerin. This paste should be applied daily for several days. Hydrogen fluoride burns have also been treated by intravenous and intracutaneous injection of 10% aqueous calcium gluconate solution.

Precautions in Handling and Storage

1. Employees should be instructed to avoid contact with liquid or gaseous hydrogen fluoride at all times, and in the appropriate procedures in case of contact.
2. Adequate emergency showers and wash-up facilities should be available in areas where hydrogen fluoride is used.
3. Eye-washing fountains should be placed in accessible locations and workers instructed in their use.
4. A hose mask, an air-line mask, or a self-contained breathing apparatus should be conveniently located in case of emergency, but in areas less likely to become contaminated.
5. Workers handling hydrogen fluoride should use full coverage of clothing at all times, rubber shoes soled with neoprene or an equally resistant material, or rubbers made of the same materials, a hat or protective head covering, a full face mask and/or chemical goggles with plastic lenses, and gauntlet-type gloves made of neoprene, plasticized polyvinyl chloride (0.028 inch thick), or an equally resistant material.
6. Leaking cylinders should be removed to the outdoors or to an isolated, well-ventilated area, and the contents transferred to other suitable containers, or disposed of in a safe manner.
7. All spillage should be flushed promptly with water. Excessive quantities of hydrogen fluoride should be neutralized with soda ash or lime before admitting wastes to drains and sewers.

8. Waste disposal of hydrogen fluoride and materials containing it depends to a great extent upon local conditions. All local, state, and federal regulations regarding health and pollution must be followed.
9. Steel cylinders for hydrogen fluoride are equipped with a special valve for discharge which should not be used as a control valve. The discharge line should include a suitable adapter for connecting the line to the cylinder valve, and a needle valve for regulating the flow of hydrogen fluoride from the cylinder. Pouring or emptying into open vessels should never be attempted. Distillation methods direct from the cylinder are not recommended. Never apply direct heat or a flame of any kind against the cylinder. Where hydrogen fluoride is discharged from the cylinder into other liquids, the delivery tube must not be passed below the surface of the liquid. A check valve should be inserted between the liquid and the cylinder. If suckback into the cylinder occurs, dangerous pressures may be formed within the cylinder. Liquid or gaseous hydrogen fluoride may be withdrawn at moderate rates from a cylinder above 19.4 °C and below 51.7 °C. This method is recommended only when small quantities are going to be used. Never apply heat directly to the cylinder to facilitate discharge. To increase withdrawal of liquid hydrogen fluoride from cylinders, the cylinder and contents should be cooled below 19.4 °C before pressurizing with *dry* compressed air or an inert gas. If it is not practicable to cool the cylinder, the operator should gauge accurately the cylinder pressure, and then introduce *dry* compressed air or inert gas at a pressure at least 34.5 kPa (5 psig) greater than the determined cylinder pressure, but in no case more than 276 kPa (40 psig). For withdrawal of liquid the cylinder should be inverted and securely fastened before use. For large rates of flow of gaseous hydrogen fluoride, liquid hydrogen fluoride may be transferred into a vaporizing process unit after cooling the boiler below the boiling point of the hydrogen fluoride. The hydrogen fluoride should not be heated over 61.1 °C. To avoid possible damage to property, full and empty cylinders should be stored separately in a sheltered isolated location, and inside operations where hydrogen fluoride is used should be segregated in a well-ventilated area.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Equipment to contain hydrogen fluoride should be pretested for leaks with *dry* compressed air or an inert gas like nitrogen. Leaks of hydrogen fluoride will be self evident since it fumes in moist air. Small leaks of hydrogen fluoride may be detected by holding an open bottle of concentrated aqueous ammonia near the suspected site of the leak. Leaks at the cylinder valve may be eliminated by tightening the stem, packing nut, or outlet cap.

Disposal of Leaking Cylinders

Leaking cylinders of hydrogen fluoride which cannot be corrected normally may be disposed of according to the procedure described in Appendix II-D.

Materials of Construction

Steel is the most widely used construction material for equipment in which hydrogen fluoride is conveyed or processed. The presence of sulfur dioxide in hydrogen fluoride increases the rate of corrosion of steel lines and equipment. Steel is also corroded readily by liquid or gaseous hydrogen fluoride at temperatures over 65 °C. Where the degree of the corrosion of steel may be considered excessive for certain applications, lines and equipment made of Monel, inconel, nickel, and copper may be used. When conditions permit the use of steel, extra heavy black seamless or welded steel pipe, having no nonmetallic inclusions, may be used. Extra heavy forged steel or slag-free welded steel fittings should be used when conditions permit the use of steel. Cast iron and malleable fittings deteriorate rapidly and should never be used. Valves for hydrogen fluoride service should preferably be of resistant alloys. However, forged steel valves with outside screw and yoke, when trimmed with resistant alloys, may be used. Valve packings made of Teflon, polyethylene, or other suitably resistant materials may be used. Lines, 2 inches or larger, should preferably be welded. Large lines, however, may be joined by flanges with suitable gasket material at the joints to prevent leakage. Threaded connections may be used on smaller size lines. Threads should be cut true to form and joints should be sealed with oil and graphite or oil and litharge applied to the threads to prevent seizing. Where gaskets are necessary, soft copper, soft annealed iron, soft silver, polyethylene, Kel-F, Teflon, or Saran may be used.

Cylinder and Valve Description

Hydrogen fluoride is shipped in DOT approved low pressure, steel cylinders. Matheson uses Compressed Gas Association (CGA) alternate standard cylinder valve outlet connection No. 660 on all cylinders in hydrogen fluoride service. The valve outlet is 1.030 inches in diameter, with right-hand external threads, flat seat and washer (see Figure 1). Lecture bottles are equipped with a special 9/16"-32 threads per inch, female outlet.

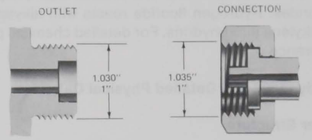


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders of hydrogen fluoride contain no safety devices; therefore, precautions should be taken to keep the cylinder from being overheated to avoid the development of dangerous hydrostatic pressures.

Recommended Controls

Cylinders of hydrogen fluoride have a very low pressure 2.1 kPa (0.3 psig). For manual flow control of the liquid and for small quantities of the gas. Matheson supplies needle valve Model 55-660, which is Teflon packed, for direct attachment

to the cylinder valve outlet. Monel needle valve Model 60L with tubing connection is recommended for use with lecture bottles.

Electronic Mass Flow Controllers

The Matheson Series 8260 of monel is designed to control the flow of gas regardless of pressure and temperature changes. This mass flow controller consists of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Hydrogen fluoride is classified by the DOT as a corrosive liquid and is shipped under the "White Label".

Commercial Preparation

Hydrogen fluoride is prepared industrially by mixing sulfuric acid with fluorspar (CaF_2) and distilling the product. The present laboratory method for preparing hydrogen fluoride consists of strongly heating purified and dried potassium hydrogen fluoride.

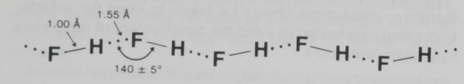
Chemical Properties

Hydrogen fluoride is thermally stable. It is strongly and highly associated both in the liquid and gaseous states. It reacts with silicates giving water and silicon tetrafluoride, with oxides and hydroxides of metals forming water and fluorides, etc. With organic compounds, it acts as a dehydrating agent, a fluorinating agent, a polymerizing agent, a powerful catalyst for condensation reactions, and a hydrolysis catalyst. Hydrogen fluoride reacts with alcohols and unsaturated compounds to form fluorides. Hydrogen fluoride reacts with alkylene oxides to give alkylene fluorohydrins. For detailed chemical properties see Reference 4.

Thermodynamic and Detailed Physical Data

Molecular Structure

Electron diffraction study of the gas (2) has shown the two hydrogen to fluorine distances to be 1.00 ± 0.06 Å and 1.55 ± 0.06 Å, the F—H·····F distance to be 2.55 ± 0.03 Å, and the F—H·····F—H·····F angle to be about 140 ± 5°, and that the polymer has a linear zig-zag configuration (shown below).



Monomeric HF has $C_{\infty v}$ symmetry, a symmetry number of one, a fundamental vibrational frequency of 4 138.32 cm^{-1} (corrected for anharmonicity of 89.88 cm^{-1}), and an H—F distance of 0.916 8 Å (0.916 8 × 10^{-10} m). The observed fundamental frequency of monomeric HF gas is 3 962 cm^{-1}. The effect of polymerization on this frequency in various phases is as follows: gas (polymer) 3 500–3 400 and 3 380–3 330 cm^{-1}; liquid 3 375 cm^{-1}; solid 3 420– 3 060 cm^{-1}.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous hydrogen fluoride.

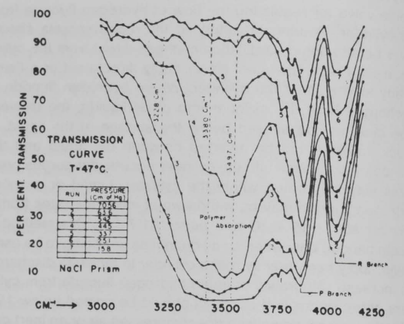


Fig. 2. Infrared spectrum of gaseous hydrogen fluoride between 3 000 and 4 250 cm^{-1}, showing the effect of pressure on polymer absorption; 125 cm copper cell, with fluorothene windows; NaCl prism; temperature: 320.15 °K (47.0 °C); pressure kPa: run 1: 94.07; run 2: 84.79; run 3: 72.26; run 4: 59.33; run 5: 44.93; run 6: 33.46; run 7: 21.06 (7).

Vapor Pressure

The vapor pressure of liquid hydrogen fluoride is represented by the Antoine vapor pressure equation (5):

$$\log_{10} p = A - \frac{B}{C + t} \quad \text{or} \quad t = \frac{B}{A - \log_{10} p} - C$$

in which t = °C and p = mmHg, and the constants A, B, and C have the values of 7.685 20, 1 478.55, and 288.22, respectively.

Some calculated vapor pressure values are shown below:

Temperature, °K	Vapor Pressure kPa	bar	mmHg
206.05	1.333	0.013	10
216.55	2.666	0.027	20
227.95	5.333	0.053	40
235.23	7.999	0.080	60
240.64	10.666	0.107	80
244.99	13.332	0.133	100
259.53	26.664	0.267	200
268.81	39.997	0.400	300
275.80	53.329	0.533	400
281.45	66.661	0.667	500
286.24	79.993	0.800	600
290.40	93.325	0.933	700

Temperature, °K	Vapor Pressure kPa	bar	mmHg
292.67	101.325	1.013	760
294.11	106.656	1.067	800
297.45	119.990	1.200	900
300.55	133.322	1.333	1 000
305.95	159.986	1.600	1 200
312.85	199.983	2.000	1 500

For additional vapor pressure values, see Table 1 and Figure 3.

Latent Heat of Vaporization, ΔHv @ 292.67 °K	6 732 J/0.020 01 kg* 7 468 J/0.020 01 kg**

* From vapor pressure vs. temperature.
** From calorimetry.

For additional ΔHv values, see Table 1.

Thermodynamic Data

Thermodynamic properties of saturated hydrogen fluoride liquid and vapor are listed in Table 1.

Thermodynamic Properties of Hydrogen Fluoride As Ideal Gas @ 25 °C (6)

Heat Capacity, C_p°	291.137 J/(mol·°K)
Entropy, S°	173.669 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ/298$	−173.699 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	8.598 kJ/mol
Enthalpy of Formation, ΔH_f°	−272.546 kJ/mol
Free Energy of Formation, ΔF_f°	−274.642 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of hydrogen fluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] S. H. Bauer, J. Y. Beach, and J. H. Simons, *J. Amer. Chem. Soc.* 61, 19 (1939).

[3] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Acid—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 83–87, Matheson, Lyndhurst, New Jersey.

[4] J. H. Simons, editor, *Fluorine Chemistry 1950*, Academic Press, Inc., New York, New York.

[5] B. J. Zwolinski, **et al.**, *Selected Values of Properties of Chemical Compounds, 1968*, Volume 1, Thermodynamic Research Center, Texas A & M University, College Station, Texas.

[6] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand; NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[7] R. D. Shelton and A. H. Nielsen, *J. Chem. Phys.* 19, 1312 (1950)

[8] J-H. Hu, D. White, and H. L. Johnston, **J. Amer. Chem. Soc.** 75, 1232–1236 (1953).

Table 1. PROPERTIES OF SATURATED VAPOR AND LIQUID HYDROGEN FLUORIDE (8)

Temperature, °K	Vapor Pressure		Specific Volume, dm^3/kg		Density, kg/dm^3		Latent Heat of Vaporization* kJ/0.020 01 kg	
	kPa	atm	Vapor	Liquid	Vapor	Liquid		
203.15	1.398	0.014		0.850		1.176		
213.15	2.533	0.025		0.870		1.149		
223.15	4.661	0.046		0.890		1.123		
233.15	7.903	0.078		0.911		1.098		
243.15	12.970	0.128		0.932		1.073		
253.15	20.680	0.204		0.954		1.048		
263.15	32.019	0.316		0.976		1.025		
273.15	48.231	0.476	465.12	0.997	0.002 15	1.003		(7.042)
283.15	71.029	0.701	396.83	1.020	0.002 52	0.980		
293.15	103.453	1.021	315.46	1.033	0.003 17	0.968	6.761	(7.473)
303.15	146.212	1.443	251.26	1.058	0.003 98	0.945	7.435	
313.15	203.359	2.007	200.80	1.078	0.004 98	0.928	8.054	
323.15	274.388	2.708	161.55	1.101	0.006 19	0.908	8.632	
333.15	370.951	3.661	130.72	1.126	0.007 65	0.888	9.176	
343.15	489.501	4.831	106.50	1.153	0.009 39	0.867	9.673	
353.15	641.39	6.33	87.41	1.185	0.011 44	0.844	10.155	
363.15	820.73	8.1	72.20	1.220	0.013 85	0.820	10.586	
373.15	1 053.8	10.4		1.256		0.796	11.008	

* From vapor pressure-temperature relation, except values in parentheses which are calorimetric.

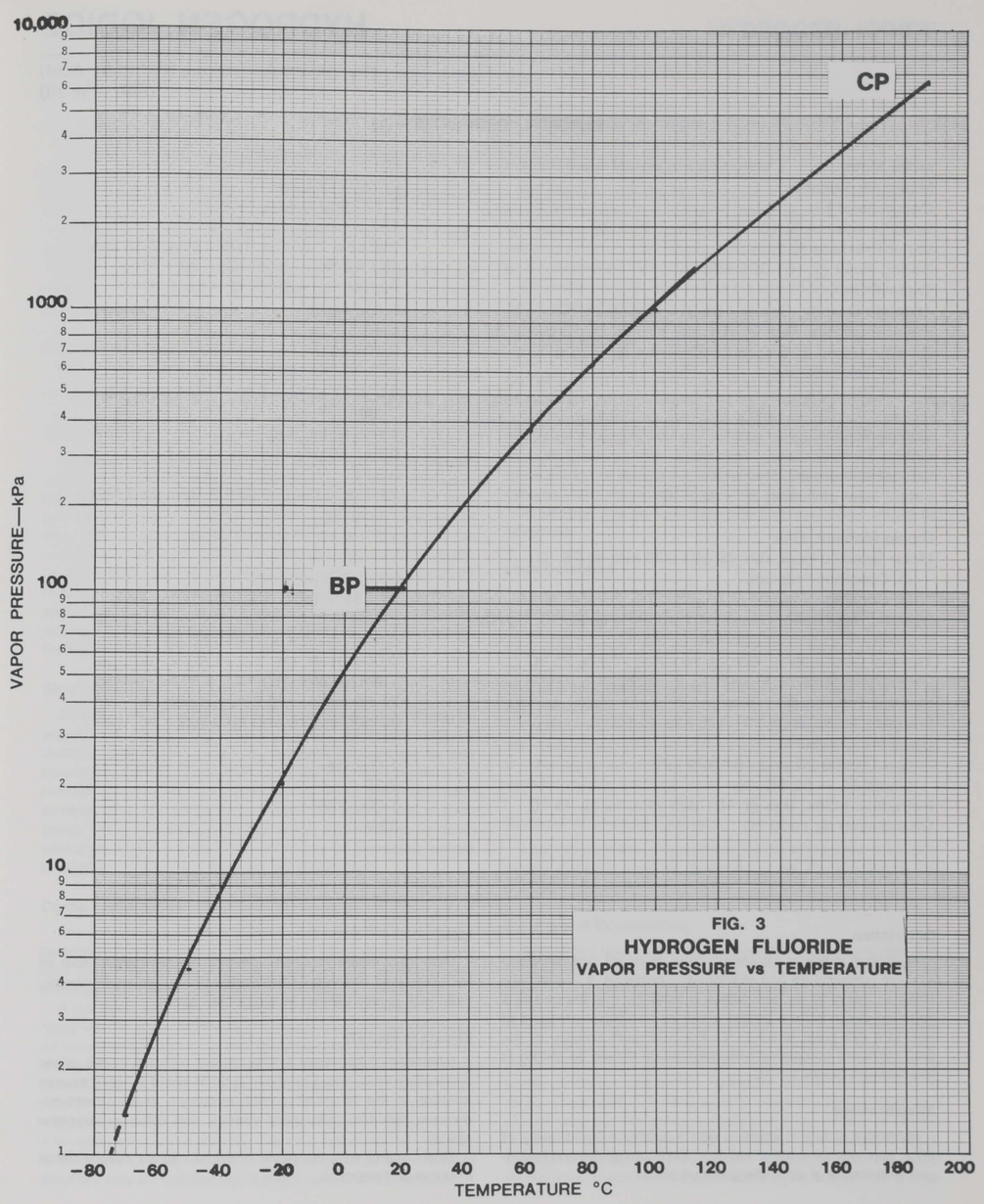


FIG. 3
HYDROGEN FLUORIDE
VAPOR PRESSURE vs TEMPERATURE

HYDROGEN IODIDE

(Synonym: Anhydrous Hydriodic Acid)
(Formula: HI)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.127 912 5 kg
One Mole of HI	0.127 912 5 kg
Specific Volume @ 101.325 kPa @ 21.1 °C	187.3 dm^3/kg; 3.0 ft^3/lb
Vapor Pressure @ 21.1 °C	756 kPa; 7.56 bar; 109.7 psia; 7.46 atm
Boiling Point @ 101.325 kPa	237.55 °K; − 35.6 °C; −32.1 °F
Triple Point	222.36 °K; −50.8 °C; −59.4 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	5.280 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	4.46
Density, Liquid @ Saturation Pressure @ −35.6 °C	2.793 kg/l
Critical Temperature	423.90 °K; 150.8 °C; 303.4 °F
Critical Pressure	8 210 kPa; 82.1 bar; 1190.4 psia; 81.0 atm
Critical Volume	1.055 4 dm^3/kg
Critical Density	0.947 5 kg/dm^3
Critical Compressibility Factor	0.314
Latent Heat of Fusion @ −50.8 °C	22.439 kJ/kg; 2 870.2 J/mol; 5.363 kcal/kg
Dipole Moment, Gas	1.27×10^{-30} C·m; 0.38 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	30.497 J/(mol·°K)
@ Constant Volume	21.784 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.40
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.016 55 mPa·s; 0.016 55 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.004 81 W/(m·°K); 11.50×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −35.6	26.69 mN/m; 26.69 dyn/cm
Solubility In Water @ 101.325 kPa @ 10 °C	42 500 cm^3/0.100 kg water
Dielectric Constant	
Gas @ 100 °C and 101.325 kPa	1.002 34
Liquid @ − 50 °C	3.39
Refractive Index, Gas @ 101.325 kPa, n_D @ 25 °C	1.000 839
Dissociation @ 1000 °C	33%

Description

Hydrogen iodide is a colorless toxic, pungent, corrosive gas at room temperature and atmospheric pressure. It is over four times as heavy as air, and fumes in most air. It is shipped as a liquefied gas in lecture bottles under its own vapor pressure of 655 kPa (95 psig) at 21.1 °C. For maximum stability of the gas, cylinders containing hydrogen iodide should be stored at temperature below 1.1 °C.

Specifications

Hydrogen iodide is shipped with a minimum liquid purity of 98%. Impurities consist of iodine in the liquid phase and hydrogen with traces of air in the gaseous phase.

Uses

Hydrogen iodide is used primarily in the manufacture of hydriodic acid and in the preparation of organic and inorganic iodides. It is also utilized as a reducing agent.

Effects in Man (2)

Inhalation of hydrogen iodide causes irritation of the upper respiratory tract, and a concentration of about 35 ppm causes irritation of the throat after short exposure. More severe exposures result in pulmonary edema, and often in laryngeal spasm.

Skin contact with the vapor or liquid causes severe tissue irritation and necrosis.

The vapors of hydrogen iodide are severely irritating to the mucous membranes of the eyes and nose.

Toxicity (2)

Concentrations of 1 000–2 000 ppm by volume in air are lethal to humans on brief exposures (up to a few minutes). Concentrations in the range of 1 000–1 300 ppm by volume in air are dangerous if breathed 30–60 minutes.

Hydrogen iodide is readily detectable in air by its sharp, penetrating odor.

No Threshold Limit Value (TLV) has been established for hydrogen iodide. A TLV of 0.1 ppm (1 mg/m^3) has been established for iodine.

First Aid Treatment (2)

The following suggested treatment should be administered at once.

Inhalation

Inhalation of moderate amounts of hydrogen iodide vapors causes choking and coughing. Exposed persons should leave the contaminated areas at once and breathe fresh air or oxygen. Severe exposure causes breathing to become labored or even stop. In such cases, the victim must be removed to an uncontaminated area and given artificial respiration (if breathing has stopped) or oxygen (if breathing is labored). The patient should be kept confortably warm, but not hot, and a physician should be called at once. Observe for signs of pulmonary edema. If lungs are affected, give antibiotics prophylactically. Rest is important.

Skin Contact

All areas of skin contacted by the hydrogen iodide should be washed off at once with running water, preferably under a drenching shower. The use of chemical neutralizers for this purpose is not recommended. Contaminated clothing must be removed at once. On severe exposure, shock symptoms such as rapid pulse, sweating, and collapse may appear and, in such cases, the victim should be kept warm and made to lie down until a physician arrives. The use of oils or ointments, unless prescribed by a physician, is not recommended.

Contact With Eyes

Any contact of hydrogen iodide vapors with the eyes should be regarded as serious. Severe irritation of the eyes and eyelids may occur if the eyes are not washed out promptly, and prolonged contact may result in impairment or loss of vision.

If the eyes are affected, they should be irrigated without delay with copious quantities of running water, preferably using an eyewash fountain. The eyelids should be spread apart with the fingers to ensure thorough rinsing. Washing should continue for at least 15 minutes. A physician, preferably an eye specialist, should be called without delay. If the physician is not available, rinsing in running water should be continued for a second period of 15 minutes. After the first period of irrigation is completed, 2 or 3 drops of pontocaine (0.5% aqueous solution) may be instilled into the eye as a first-aid measure.

Nose

If the mucous membranes of the nose are irritated, rinse with water for at least 15 minutes.

Precautions in Handling and Storage

(a) Workers who handle hydrogen iodide should wear protective clothing such as rubber or plastic aprons, rubber gloves, and suitable gas-tight chemical safety goggles. Woolen outside clothing or other acid resistant fabrics are recommended for workers handling hydrogen iodide.

(b) Instant-acting safety-showers should be available in the event of an emergency.

(c) Special eye-washing fountains or similar equipment should be available for eye irrigation.

(d) Proper respiratory equipment must be provided and personnel wearing such equipment must be carefully instructed in its operation and limitations.

(e) Precautions should always be taken to prevent suckback of foreign materials into the cylinder by using a check valve, vacuum break, or trap, since such a setback may cause the development of dangerous pressures within the cylinder. The cylinder valve should be closed after each use.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Large leaks of hydrogen iodide will be evident by the formation of dense white fumes on contact with the atmosphere. Small leaks of hydrogen iodide may be detected by holding an open bottle of concentrated ammonium hydroxide solution near the site of the suspected leak (formation of dense white fumes). Wet blue litmus paper will turn pink when exposed to a hydrogen iodide leak.

Cylinder valve leaks can usually be corrected by tightening the valve packing nut (turn clockwise as viewed from above). If valve leaks persist or leaks appear at any portion of the cylinder, advise the supplier immediately.

Disposal of Leaking Cylinders

Leaking cylinders of hydrogen iodide which cannot be corrected normally may be disposed of by the procedure described in Appendix II-D.

Materials of Construction

Anhydrous hydrogen iodide is essentially inert to metals and does not attack the commonly used structural metals (stainless steel, mild steel) under normal conditions of use (room temperature and atmospheric pressure). In the presence of moisture, however, hydrogen iodide will corrode most metals other than silver, platinum, and tantalum; carbon, graphite, and impregnated carbon and graphite are recommended materials of construction for wet or dry hydrogen iodide. When used at higher pressures, it is necessary to use extra heavy black iron pipe throughout. No galvanized pipe or brass or bronze fittings should be used as these will corrode. High pressure steel, monel, or aluminum-iron-bronze valves should be used throughout. Users of hydrogen iodide are warned to always

shut off their hydrogen iodide lines from the use end, backward to the cylinders.

Cylinder and Valve Description

Lecture bottles containing hydrogen iodide have a special 5/16-inch-32 threads per inch, female outlets.

Recommended Controls

Manual Controls

A Model 60L Monel needle valve with ¼ inch Monel tubing outlet is available for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory Monel flowmeter units with 150 mm tubes and floats are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, with Monel transducers, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8260 of Monel is designed to control the flow of gas regardless of pressure and temperature changes. This mass flow controller consists of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Hydrogen iodide is classified by the D.O.T. as a nonflammable gas and is shipped under "Green Label".

Chemical Preparation

Hydrogen iodide is prepared (1) by chemical combination of its elements, (2) by adding water dropwise to a mixture of red phosphorus and iodine, (3) by adding concentrated aqueous hydrogen iodide to phosphorous pentoxide, and (4) by adding iodine dissolved in 57% aqueous hydrogen iodide to red phosphorus.

Chemical Properties

Hydrogen iodide is decomposed by light. It is the least stable of the hydrogen halides. Even at room temperature it dissociates slightly into its constituents. Chlorine and bromine vapor displace the iodine from hydrogen iodide. In aqueous solution hydrogen iodide is wholly in the ionic form. Aqueous hydrogen iodide is easily oxidized; it is slowly affected even by atmospheric oxygen. Chlorine water or bromine water displaces the iodine when added to aqueous hydrogen iodide. Hydrogen iodide forms hydriodides with organic bases. Hydrogen iodide reacts with the lower aliphatic alcohols, forming the corresponding iodo compounds.

Thermodynamic and Detailed Physical Data

Molecular Structure

The linear, heteropolar hydrogen iodide molecule has $C_{\infty v}$ symmetry, a symmetry number of one, and an H—I bond distance of 1.62 Å (1.62×10^{-10} m).

Infrared Spectrum

See Figure 1 for the infrared spectrum of gaseous hydrogen iodide.

Vapor Pressure

The vapor pressure of liquid hydrogen iodide up to 200 kPa (1 500 mmHg) follows the Antoine vapor pressure equation (3).

$$\log_{10} p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 5.608 9, 416.04, 188.1, respectively.

The following vapor pressure values have been calculated by this equation (3).

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
214.65	33.326	333.3	250
217.85	39.993	400.0	300
223.45	53.327	533.3	400
228.05	66.652	666.6	500
232.05	79.986	800.0	600
235.55	93.320	933.2	700
237.55	101.325	1 013.25	760
238.85	106.655	1 067	800
241.75	119.989	1 200	900
244.55	133.313	1 333	1 000
249.55	159.982	1 600	1 200
256.05	199.975	2 000	1 500

The vapor pressure of liquid hydrogen iodide above 202.650 kPa (2 atm) is shown below (4).

Temperature, °K	Vapor Pressure kPa	bar	atm
280.45	506.625	5.07	5
305.15	1 013.250	10.1	10
335.35	2 026.500	20.3	20
373.85	4 053.000	40.5	40
400.65	6 079.500	60.8	60
423.90 (C.T.)	8 207.325	82.1	81 (3)

See Figure 2 for vapor pressure curve.

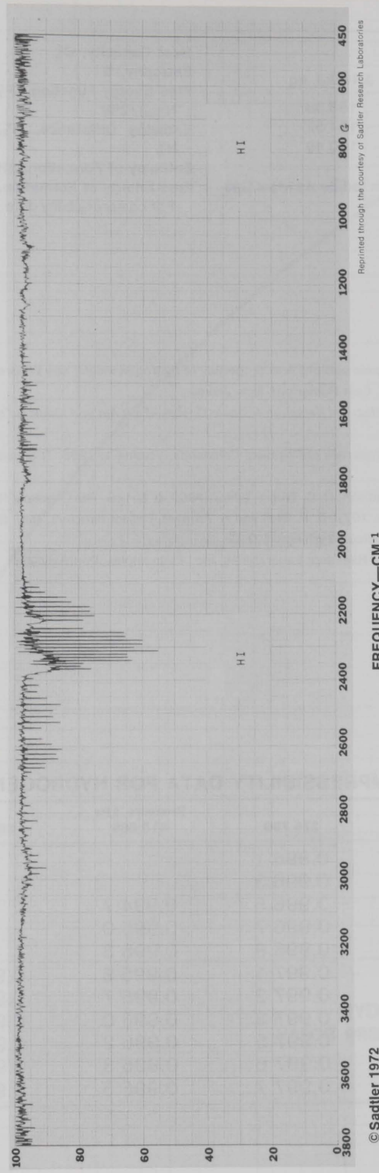


Fig. 1. Infrared spectrum of gaseous hydrogen iodide over the frequency region of 3 800 cm^{-1} to 450 cm^{-1}; 100 cm path length cell, with KBr windows; cell pressure (complete scan): 66.66 kPa (500 mmHg) (6).

HYDROGEN IODIDE

Latent Heat of Vaporization, ΔHv

Temperature, °C	ΔHv, kJ, kg
−48.0	158.38
−35.6	154.52
−23.0	150.49

Thermodynamic Properties of Hydrogen Iodide As Ideal Gas @ 25 °C (5)

Heat Capacity, C°_p	29.158 J/(mol·°K)
Entropy, S°	206.485 J/(mol·°K)
Free Energy Function, $(F^\circ_{298} - H^\circ_{298})/298$	−206.485 J/(mol·°K)
Enthalpy Difference, $H^\circ_{298} - H^\circ_0$	8.657 kJ/mol
Enthalpy of Formation, ΔH°_f	26.359 kJ/mol
Free Energy of Formation, ΔF°_f	1.573 kJ/mol

For compressibility data, see Table 1.

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of hydrogen iodide, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 87-91, Matheson, Lyndhurst, New Jersey.

[3] B. J. Zwolinski, et al., *Selected Values of Properties of Chemical Comounds*, Volume 1, *1968*, Thermodynamic Research Center, Texas A & M University, College Station, Texas.

[4] *Handbook of Chemistry and Physics*, 50th edition, R. C. Weast, editor, *1969*, p. D-145, The Chemical Rubber Co., Cleveland, Ohio.

[5] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data. Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[6] *The Sadtler Standard Spectra*, 1972, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Table 1. COMPRESSIBILITY DATA FOR HYDROGEN IODIDE

Temperature, °K	Pressure, kPa 137.895	275.790	413.685	689.476	1 378.951
266.48	0.998 1	0.996 1			
272.04	0.998 2	0.996 3			
277.59	0.998 3	0.996 5	0.994 7		
283.15	0.998 4	0.996 7	0.995 0		
288.71	0.998 5	0.996 9	0.995 3		
294.26	0.998 5	0.997 1	0.995 5	0.992 3	
299.82	0.998 6	0.997 2	0.995 7	0.992 7	
305.37	0.998 7	0.997 3	0.996 0	0.993 1	
310.93	0.998 7	0.997 5	0.996 2	0.993 4	
316.48	0.998 8	0.997 6	0.996 3	0.993 7	
322.04	0.998 9	0.997 7	0.996 5	0.994 0	0.987 4

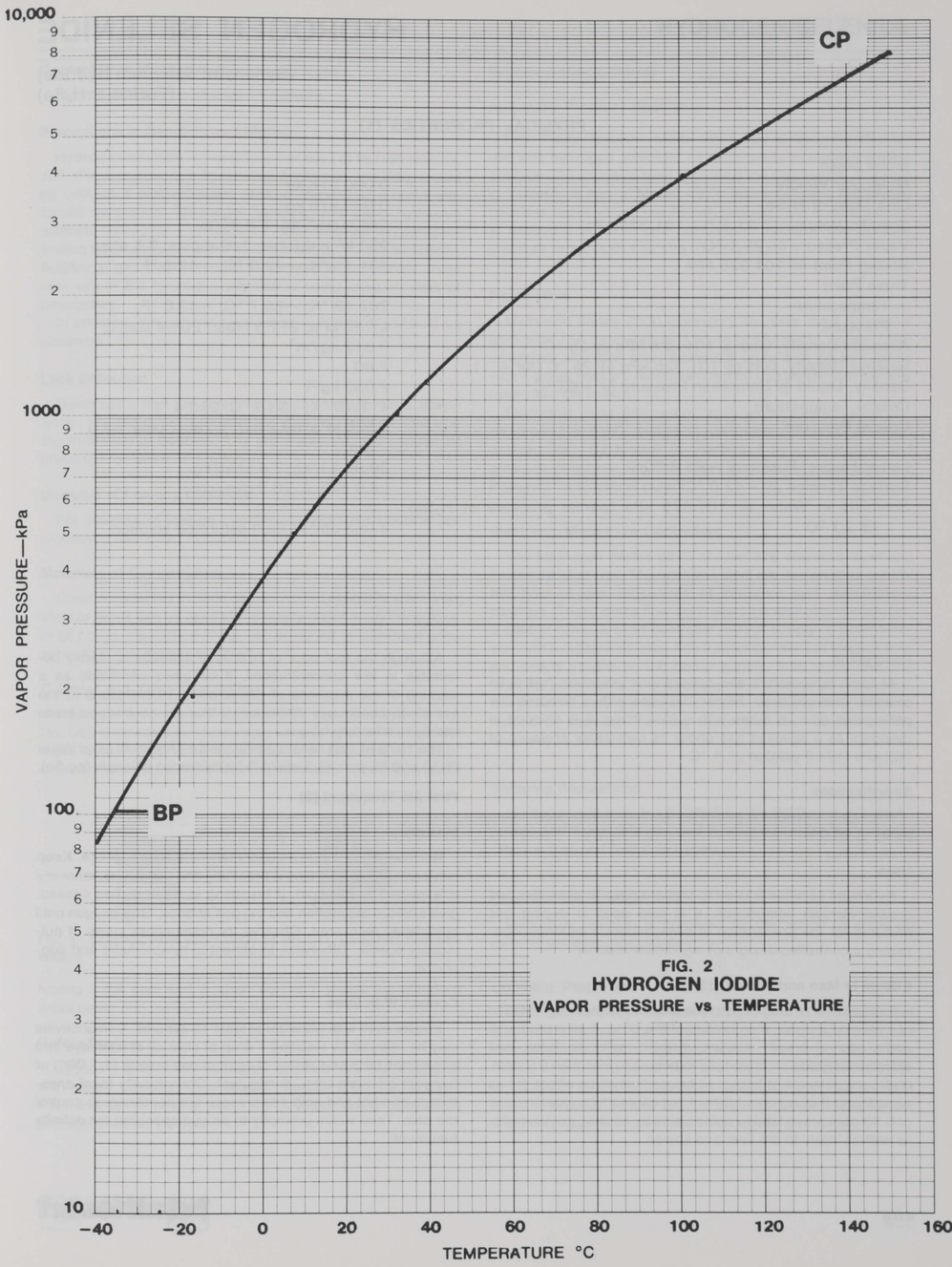


FIG. 2
HYDROGEN IODIDE
VAPOR PRESSURE vs TEMPERATURE

HYDROGEN SELENIDE

(Synonym: Selenium Hydride)
(Formula: H_2Se)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.080 976 kg
One Mole of H_2Se	0.080 976 kg
Specific Volume @ 21.1 °C, 101.325 kPa	299.6 dm^3/kg; 4.8 ft^3/lb
Vapor Pressure @ 21.1 °C	960 kPa; 9.6 bar; 139.6 psia; 9.5 atm
Boiling Point @ 101.325 kPa	231.15 °K; −42.0 °C; −43.6 °F
Triple Point	
Temperature	207.42 °K; −65.7 °C; −43.6 °F
Pressure	27.25 kPa; 272.5 mbar; 204.4 mmHg
Absolute Density, Gas @ 101.325 kPa @ 25 °C	3.312 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	2.80
Density, Liquid @ Saturation Pressure @ −63 °C	2.039 kg/l
Critical Temperature	411.15 °K; 138.0 °C; 280.4 °F
Critical Pressure	8 920 kPa; 89.2 bar; 1 293.2 psia; 88.0 atm
Latent Heat of Fusion @ −65.7 °C	30.96 kJ/kg; 7.4 kcal/kg
Surface Tension @ −42.0 °C	28.9 mPa.s; 28.9 dyn/cm
Solubility In Water @ 101.325 kPa (partial pressure of H_2Se) @ 20 °C	2.052 dm^3 H_2Se/l saturated solution

Description

At room temperature and atmospheric pressure, hydrogen selenide is a colorless, highly toxic gas with a disagreeable penetrating odor. It burns with a blue flame. It is shipped in cylinders as a liquefied gas under its own vapor pressure of 862 kPa (124.9 psig) at 21.1 °C.

Specifications

Hydrogen selenide supplied by Matheson has a minimum purity of 98.0%.

Uses

Hydrogen selenide is used to prepare metallic selenides and organoselenium compounds. It is also used in doping gas mixtures for the preparation of semiconductor materials containing a controlled amount of significant impurity.

Effects In Man and Toxicity (2)

Exposure to hydrogen selenide produces moderate irritation of eyes and mucous membranes of the nose. It also produces garlic odor of breath, nausea, metallic taste, dizziness, and extreme lassitude on prolonged exposure to less than 0.2 ppm. Hydrogen selenide is known to have a hemolytic effect. It has been found that repeated 8-hour exposures to concentrations of 0.03 ppm prove fatal to guinea pigs by causing pneumonitis, as well as injury to the liver and spleen.

Although the foul odor of hydrogen selenide is readily detectable in low concentrations, it becomes unreliable as a warning of the presence of dangerous concentrations of the gas since continuous inhalation of low concentrations leads rapidly to olfactory fatigue.

The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 0.05 ppm (0.2 mg/m^3) for hydrogen selenide (as Se).

First Aid Treatment (2)

Inhalation

Remove the victim to an uncontaminated atmosphere. Keep him warm and at rest. If he is breathing and conscious, recovery is expected to be rapid. If breathing is weak or has ceased, give artificial respiration and oxygen at once. Give oxygen until completely recovered. Observe for premonitory signs of pulmonary edema. Otherwise treatment is symptomatic and supportive.

Contact With Eyes

Irrigate eyes with water for at least 15 minutes. Conjunctivitis may be relieved by instilling 1 drop of olive oil in each eye and sometimes by 3 or 4 drops of epinephrine sulfate (1:1 000) at frequent intervals (e.g., 5 minutes). Occasionally local anesthetics and hot and cold compresses are necessary to control the pain. Take victim promptly to an eye specialist for definite treatment.

Contact With Mucous Membranes of Nose

Flush with water for at least 15 minutes.

Precautions in Handling and Storage

Hydrogen selenide is hazardous because of its high toxicity, and also because it is flammable. Hydrogen selenide should be used in a well-ventilated area, preferably in a hood with forced ventilation. Personnel handling and using hydrogen selenide should have available for immediate use oxygen generating gas masks or masks having a self-contained air supply. Additional gas masks should be located in convenient areas near where the hydrogen selenide is being used, in case of emergency.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Never use a flame to detect hydrogen selenide leaks. Soapy water, painted over the suspected area, will indicate leaks by the formation of bubbles. It is preferable that the system be pretested for leaks with nitrogen.

Disposal of Leaking Cylinders

For disposal of leaking cylinders of hydrogen selenide see procedure described in Appendix II-D.

Materials of Construction

Class A materials include aluminum and stainless steel. Iron, steel or brass can be used successfully under many conditions. In all cases, equipment should be designed to withstand pressures that may be encountered.

Cylinder and Valve Description

Hydrogen selenide is shipped in DOT approved cylinders. A No. 660 stainless steel diaphragm valve is used as the cylinder valve outlet. This valve outlet has a thread size of 1.030″ diameter with right-hand external threads, with a connector

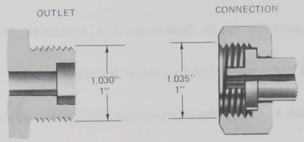


Fig. 1. CONNECTION 660 1.030″-14 RH EXT. using Flat Seat with Washer

having a flat seat and washer. Figure 1 shows the standard valve outlet and mating connection.

Safety Devices

Cylinders containing hydrogen selenide are not equipped with safety devices. They should, therefore, be stored away from sources of heat to avoid the development of dangerous pressures within the cylinder.

Recommended Controls

Automatic Pressure Regulator

High Purity Regulator Model 3501-660 is recommended for use with hydrogen selenide. All metal parts in the gas stream are type 316 stainless steel, including the diaphragm. The seat is Tefzel®. It has a Model 4374 stainless steel diaphragm packless outlet valve. The helium leakage rate is certified not to exceed 2×10^{-10} cm^3 per second inboard. The delivery pressure range is 0–172 kPa (0–25 psig).

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Hydrogen selenide is classified by the DOT as a "Class A" poison and flammable gas and is shipped under the required "Poison Gas and Red Gas Labels".

Chemical Preparation

Hydrogen selenide is prepared by the action of acids on metallic selenide, e.g., Al_2Se_3.

Chemical Properties

Hydrogen selenide is a weak acid and both its soluble normal and acid salts are, therefore, strongly hydrolyzed. It is less thermally stable than hydrogen sulfide, decomposing to elemental selenium at about 160°C. It may be converted to K_2Se or KSeH in alcoholic potassium hydroxide and reacted with reactive organic halides to give organoselenium compounds. If ignited, it burns to give selenium dioxide and water.

Thermodynamic and Detailed Physical Data

Molecular Structure (1)

Hydrogen selenide is a bent molecule having C_{2v} symmetry, a symmetry number of two; it has a Se-H bond distance of 1.47 Å (1.47×10^{-10} m) and a H-Se-H bond angle of 91°.

Infrared Spectrum

Hydrogen selenide is both infrared and Raman active and the gas shows the following three fundamental vibrational frequencies in its infrared spectrum: 2 345, 1 034, and 2 358 cm^{-1}.

Vapor Pressure (3)

The vapor pressure of liquid hydrogen selenide follows the following Antoine vapor pressure equation between 206.95°K and 246.15°K.

$$\log_{10}p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10}p} - C$$

in which the constants A, B, and C have the values of 6.966 0, 787.67, and 235.0, respectively, and p = mmHg and t = °C. Some calculated values are shown below.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
206.95	26.659	266.6	200
210.55	33.326	333.3	250
213.65	39.993	400.0	300
218.65	53.327	533.3	400
222.75	66.652	666.6	500
226.25	79.986	800.0	600
229.15	93.320	933.3	700
231.15	101.325	1 013.25	760
232.15	106.655	1 067	800
234.15	119.989	1 200	900
237.15	133.313	1 333	1 000
241.15	159.982	1 600	1 200
246.15	199.975	2 000	1 500

Latent Heat of Vaporization, △Hv

Temperature, °C	△Hv, kJ/kg
−53.15	251.12
−42.0	245.33
−33.15	240.69

Thermodynamic Properties of Hydrogen Selenide As Ideal Gas @ 25°C (4)

Heat Capacity, C_p°	34.752 J/(mol·°K)
Entrapy, S°	219.020 J/(mol·°K)
Free Energy Function, $(G_{298}^\circ - H_0^\circ)/298$	−185.456 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$ (5)	10.004 kJ/mol
Enthalpy of Formation, $\triangle H_f^\circ$ (5)	29.71 kJ/mol
Gibbs Energy of Formation, $\triangle G_f^\circ$ (5)	15.90 kJ/mol

For compressibility data for hydrogen selenide, see Table 1.

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of hydrogen selenide, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 75–83, Matheson, Lyndhurst, New Jersey.

[3] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds*, Volume 1, *1968*, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[4] J. S. Gordon, *J. Chem. Eng. Data 14*, 460 (1969).

[5] D. D. Wagman, *et al.*, *Selected Values of Chemical Thermodynamic Properties*, Natl. Bur. Stand. Tech. Note 270-3, *1968*, p. 56, U. S. Government Printing Office, Washington, D. C.

Table 1. COMPRESSIBILITY DATA FOR HYDROGEN SELENIDE

Temperature, °K	Pressure, kPa 137.895	275.790	413.685	689.476	1 378.951
266.48	0.988 5	0.996 9			
272.04	0.998 6	0.997 1	0.995 6		
277.59	0.998 6	0.997 2	0.995 8		
283.15	0.998 7	0.997 4	0.996 0		
288.71	0.998 8	0.997 5	0.996 2	0.993 6	
294.26	0.998 8	0.997 6	0.996 4	0.993 8	
299.82	0.998 9	0.997 7	0.996 6	0.994 2	
305.37	0.998 9	0.997 8	0.996 7	0.994 4	
310.93	0.999 0	0.997 9	0.996 9	0.994 7	0.988 9
316.48	0.999 0	0.998 0	0.997 0	0.995 0	0.989 4
322.04	0.999 1	0.998 1	0.997 2	0.995 2	0.989 9

HYDROGEN SULFIDE

(Formula: H_2S)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.034 076 kg
One Mole of H_2S	0.034 076 kg
Specific Volume @ 21.1 °C, 101.325 kPa	70.11 dm^3/kg; 11.23 ft^3/lb
Vapor Pressure @ 21.1 °C	1 840 kPa; 18.4 bar; 266.7 psia; 18.15 atm
Boiling Point @ 101.325 kPa	212.81 °K; −60.3 °C; −76.6 °F
Triple Point	187.62 °K; −85.5 °C; −122.0 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	1.406 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.188
Density, Liquid @ Saturation Pressure @ −60.3 °C	0.960 kg/l
Critical Temperature	373.56 °K; 100.4 °C; 212.7 °F
Critical Pressure	9 010 kPa; 90.1 bar; 1 306.5 psia; 88.9 atm
Critical Volume	2.867 dm^3/kg
Critical Density	0.349 kg/dm^3
Critical Compressibility Factor	0.283
Latent Heat of Fusion @ −85.5 °C	2 376.5 J/mol; 69 741.2 J/kg; 16.67 kcal/kg
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	34.218 J/(mol·°K)
@ Constant Volume	25.806 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.33
Flammability Limits In Air	4.3–46.0% (by volume)
Dipole Moment, Gas	3.669×10^{-30} C·m; 1.10 D
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.012 8 mPa.s; 0.012 8 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 15.6 °C	0.014 004 W/(m·°K); 33.5×10^{-6} cal·cm/(s·cm^2·°C)
Solubility In Water @ 101.325 kPa @ 25 °C	2.257 cm^3/1 cm^3 water
Autoignition Temperature	533.15 °K; 260.0 °C; 500 °F
Index of Refraction, Gas @ 101.325 kPa, n_D @ 25 °C	1.000 584 5
Dielectric Constant	
Gas @ 0 °C, 101.325 kPa	1.004
Liquid @ −78.5 °C	9.05

Description

At room temperature and atmospheric pressure, hydrogen sulfide is a colorless, flammable, toxic gas having an offensive odor described as that of rotten eggs. It is shipped in steel cylinders as a liquefied gas under its own vapor pressure of 1 737 kPa (252 psig) at 21.1 °C.

Specifications

Matheson supplies two grades of hydrogen sulfide as follows:

1. C.P. Grade

This grade of hydrogen sulfide has a minimum purity of 99.5% (liquid phase).

2. Technical Grade

This grade has a minimum purity of 99.0% (liquid phase).

Uses

Hydrogen sulfide is used in metallurgy for the preparation of metallic sulfides. It is also used in the preparation of phosphors, oil additives, and as an analytical reagent in chemical analysis. It is also used in metals separation, removal of metallic impurities, and preparation of metallic sulfides in analytical laboratories; and for reaction with numerous functional organic compounds.

Effects in Man and Toxicity (2)

In concentrations of 20 to 50 ppm, hydrogen sulfide irritates the eyes. Slightly higher concentrations irritate the upper respiratory tract and, if prolonged, may result in pulmonary edema. Inhalation of 500 ppm for 30 minutes produces headache, dizziness, excitement, staggering, and gastroenteric disorders, followed in some cases by bronchitis or bronchial pneumonia. Concentrations above 600 ppm can be fatal within 30 minutes through respiratory paralysis.

Although the foul odor of hydrogen sulfide is readily detectable in low concentrations, it becomes unreliable as a warning of dangerous concentrations of gas since continuous inhalation leads rapidly to olfactory fatigue.

The 1979 ACGIH has established a Threshold Limit Value (TLV) of 10 ppm (15 mg/m^3) for hydrogen sulfide.

Matheson

First Aid Treatment (2)

INHALATION

Remove the victim to an uncontaminated atmosphere. Keep him warm and at rest. If he is breathing and conscious, recovery is expected to be rapid. If breathing is weak or has ceased, give artificial respiration and oxygen at once. Give oxygen until completely recovered. Observe for premonitory signs of pulmonary edema. Otherwise treatment is symptomatic and supportive.

Contact with Eyes

Irrigate eyes with water for at least 15 minutes. Conjunctivitis may be relieved by instilling 1 drop of olive oil in each eye and sometimes by 3 or 4 drops of epinephrine sulfate (1:1 000) at frequent intervals (e.g., 5 minutes). Occasionally local anesthetics and hot and cold compresses are necessary to control the pain. Take victim promptly to an eye specialist for definite treatment.

Contact with Skin and Mucous Membranes of Nose

Flush with water for at least 15 minutes.

Precautions in Handling and Storage

The major hazards in the handling of hydrogen sulfide arise from its toxicity and flammability. The gas should, therefore, be used in a well-ventilated area, preferably a hood, and flames, sparks, and sources of excessive heat should be kept out of the area in which hydrogen sulfide is stored or used. The sense of smell should not be depended upon to detect dangerous concentrations of hydrogen sulfide and some supplementary means of detection should be used (see section on Leak Detection).

Personnel using hydrogen sulfide should work in pairs. They should wear for instantaneous use a gas mask with an all-purpose canister or a light three-minute unit with a self-contained air supply, which can be donned quickly before evacuating the area. Operators should carry wet lead acetate paper (turns black in the presence of minute amounts of hydrogen sulfide) on their wrists or belt for detection of dangerous concentrations of gas. In addition, there should be provided multipoint air samplers with alarms for plant production units to constantly monitor the air in and around the units.

Further, the following specific precautions should be observed:

1. Do not store reserve stocks of hydrogen sulfide cylinders with cylinders containing oxygen or other highly oxidizing or combustible materials.
2. Ground all lines and equipment used with hydrogen sulfide.
3. Use check valves or traps to prevent suckback into the cylinder.
4. Use a cylinder size which can be conveniently emptied in a reasonably short amount of time.
5. Keep gas masks approved for hydrogen sulfide service in an area not likely to be contaminated, ready for use in case of emergency.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks may be detected by painting the suspected area with a soap solution, or cadmium chloride solution (turns yellow upon contact with hydrogen sulfide). It is also possible to detect leaks with moist lead acetate paper. A number of automatic gas analyzer equipment manufacturers can supply hydrogen sulfide warning detectors for very low concentrations. Matheson has a manual Toxic Gas Detector, Model 8014 K, for detection of hydrogen sulfide in various concentrations with the following detector tubes: No. 120SA (0.01–0.2%); 120SB (0.75–150 ppm); 120SC (0.005–0.16%, but in the presence of sulfur dioxide); and 120SH (0.02–0.3%). The detector tubes contain a chemical reagent which reacts with the hydrogen sulfide. A color stain is produced which varies in length with the concentration. The length of the stain, and hence the concentration, is read directly from the tube.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-D.

Materials of Construction

Aluminum is considered a Class A material of construction for wet or dry hydrogen sulfide. Since aluminum may not always have the strength properties required, type 316 stainless steel can be substituted with success. For dry hydrogen sulfide black iron or steel piping can be used satisfactorily. Brass, although tarnished by dry hydrogen sulfide, does not seem to be adversely affected. Brass regulators used in dry hydrogen sulfide service have stood up for years with no appreciable malfunctioning or signs of corrosion.

Cylinder and Valve Description

Hydrogen sulfide cylinder valves are made of a special forged bronze alloy and are packed with Teflon. The outlet is designated as connection No. 330. Thread specifications are: 0.825 inch diameter-14 threads per inch, left-hand external. The connection is sealed on a flat seat by use of a washer. This outlet is designated as the approved standard for hydrogen sulfide by the Compressed Gas Association (CGA) (see Figure 1 for drawing and specifications on this valve outlet and its mating connection). Lecture bottles have a special $^5/_{16}$ inch-32 threads per inch, female valve outlet.

Hydrogen sulfide is packaged by Matheson in DOT approved, high pressure steel cylinders.

Matheson

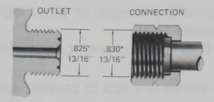


Fig. 1. CONNECTION 330 .825″-14 LH EXT. used with Flat Seat and Washer

Safety Devices

Safety devices required by the DOT and approved by The Bureau of Explosives are required in hydrogen sulfide service, but are prohibited on DOT 106-A800X containers. The type approved is fusible metal having a melting point of approximately 73.9 °C (165 °F). When the cylinder is over 30 inches long, this type of device is required in both ends of the cylinder. When this device is placed in a valve it must either be poured into the valve, making it inaccessible, or put into a round plug which screws into the back of the valve. Due to the fact that many of the fusible devices in hydrogen sulfide cylinder valves were developing pin-hole leaks, Matheson has gained approval from the Bureau of Explosives to ship cylinders with valves having safety devices containing a frangible disc which is backed up by a fusible metal. This frangible disc is gold plated, and prevents any corrosion from taking place at the interface between the valve body and the fusible metal, thus preventing leaks from developing.

Recommended Controls

Automatic Pressure Regulators

The cylinder pressure of hydrogen sulfide can be reduced to a safe working value by means of a single stage pressure regulator. Matheson supplies a regulator designated as Model 11-330 which will reduce hydrogen sulfide pressure to delivery pressures of 28–550 kPa (4–80 psig) regulator is constructed of an anodized aluminum body with type 316 stainless steel internal parts. The diaphragm is FEP Teflon on Neoprene and the seat is Teflon. The regulator is equipped with one gauge to show delivery pressure. No tank gauge is provided since the cylinder pressure of hydrogen sulfide will remain constant as long as liquid remains in the cylinder. It is necessary to determine the content of a hydrogen sulfide cylinder by weight.

For accurate and very sensitive low pressure control, Matheson has available regulator Model 71-330, which will afford a delivery pressure range of 3.5-34.5 kPa (0.5–5.0 p.s.i.g). A Model No. 71A-330 has a delivery pressure range of 34.5–69 kPa (5–10 p.s.i.g). These regulators have an oversize pancake body of aluminum, a Teflon-faced Butyl rubber diaphragm, a Teflon seat, and internal parts of 303 stainless steel.

Manual Controls

Where manual flow controls can be used, Matheson Model-330 of 303 stainless steel with ¼ inch tube fitting is recommended for use with C.P. Grade hydrogen sulfide and No. 50A-330 for use with Technical Grade hydrogen sulfide. A No. 32S stainless steel control valve is available for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ±1.2%.

Shipping Regulations

Hydrogen sulfide is shipped in DOT approved steel cylinders as a flammable compressed gas taking a DOT "Red Gas Label".

Commercial Preparations

Hydrogen sulfide occurs as a by-product from many chemical processes. It is an off-gas in the production of viscose rayon, synthetic rubber, and various petroleum products, dyes, and leather processing. It can also be manufactured by treatment of many metallic sulfides with a mineral acid such as hydrochloric or sulfuric acid.

Chemical Properties

Hydrogen sulfide in aqueous solution is a weak diprotic acid. A solution of hydrogen sulfide is slowly oxidized to sulfur and water by the action of dissolved oxygen. Hydrogen sulfide is a reducing agent in acid and in alkaline solution. Hydrogen sulfide forms metallic sulfides, especially with heavy metals, by passing hydrogen sulfide through solutions of the metal salts. Hydrogen sulfide adds to ethylenic bonds to form mercaptans when heated under pressure with HF, BF_3, or H_2SO_4 as catalysts. Acetylene and hydrogen sulfide condense to form thiophene under suitable conditions (high temperature and catalysis). Hydrogen sulfide also reacts with many other organic compounds.

Thermodynamic and Detailed Physical Data

Molecular Structure

Hydrogen sulfide is a bent molecule, with C_{2v} symmetry, a symmetry number of one, an S-H bond distance of 1.328 Å (1.328×10^{-10} m) and an H-S-H bond angle of 92.2°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous hydrogen sulfide.

Vapor Pressure

The vapor pressure of liquid hydrogen sulfide between 179.87 and 227.25 °K is expressed by the following Antoine vapor pressure equation (3).

$$\log_{10} p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which the constants A, B, and C have the values of 6.993 92, 768.130 2, and 247.093, respectively, and p = mmHg and t = °C.

The following vapor pressure values have been calculated by this equation:

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
179.87	13.334	133.3	100
185.49	20.002	200.0	150
189.74	26.669	266.7	200
193.19	33.336	333.4	250
196.118	40.003	400.0	300
200.956	53.338	533.4	400
204.902	66.672	666.7	500
208.261	80.006	800.1	600
211.201	93.341	933.4	700
212.809	101.325	1 013.25	760
213.826	106.675	1 067	800
216.21	120.009	1 200	900
218.38	133.344	1 333	1000
222.27	160.013	1 600	1200
227.25	200.16	2 002	1500

The vapor pressure of liquid hydrogen sulfide from the boiling point to the critical point is shown below (4).

Temperature, ° K	Vapor Pressure kPa	bar	atm
212.81 (B.P.)	101.3	1.013	1
273.15	1 090	10.9	10.8
283.15	1 430	14.3	14.1
293.15	1 880	18.8	18.5
303.15	2 390	23.9	23.6
313.15	3 010	30.1	29.7
323.15	3 700	37.0	36.5
333.15	4 510	45.1	44.5
343.15	5 380	53.8	53.1
353.15	6 480	64.8	64.0
363.15	7 360	73.6	72.6
373.15	8 990	89.9	88.7
373.56 (C.T.)	9 010	90.1 (C.P.)	88.9 (C.P.)

For vapor pressure values at other temperatures, see Figure 3 (vapor pressure curve).

Latent Heat of Vaporization, △Hv

Temperature, °C	△Hv, kJ/mol
−100	20.318
−80	19.514
−60.3	18.673

Thermodynamic Data

For thermodynamic properties of saturated and superheated hydrogen sulfide, see Tables 1 and 2, respectively.

Thermodynamic Properties of Hydrogen Sulfide As Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	34.192 J/(mol·°K)
Entropy, S°	205.648 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−205.648 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	9.962 kJ/mol
Enthalpy of Formation, $\triangle H_f^\circ$	−20.418 kJ/mol
Free Energy of Formation, $\triangle F_f^\circ$	−33.284 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of hydrogen sulfide, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 75–83, Matheson, Lyndhurst, New Jersey.

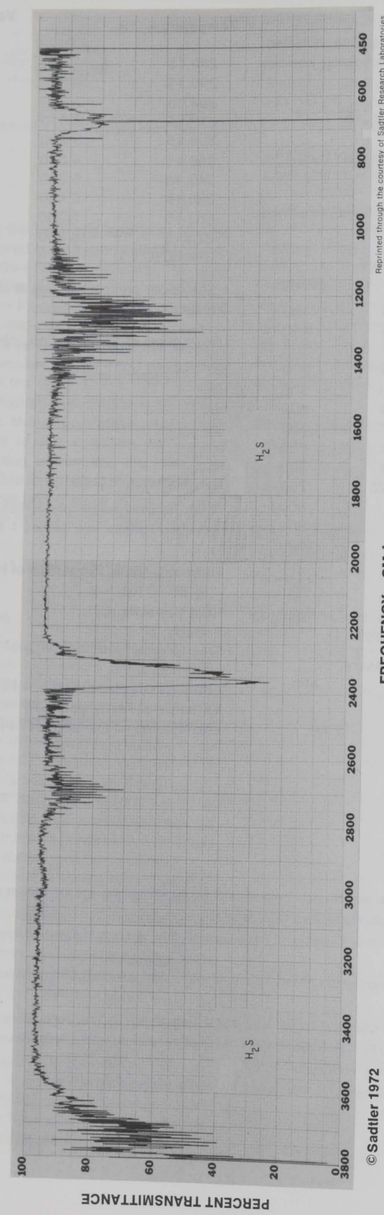
[3] B. J. Zwolinski, **et al.**, *Selected Values of Properties of Chemical Compounds, 1968*, Volume 1, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[4] P. Macaluso in Kirk-Othmer's *Encyclopedia of Chemical Technology, 1969*, Volume 19, p. 376, John Wiley & Sons, Inc., New York, New York.

[5] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[6] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[7] J. R. West, *Chem. Eng. Progr.* 44, 287 (1948).



Reprinted through the courtesy of Sadtler Research Laboratories
© Sadtler 1972

Fig. 2. Infrared spectrum of gaseous hydrogen sulfide over the frequency region of 3 800 cm^{-1} to 450 cm^{-1}; 100 cm path length cell, with KBr windows; cell pressure (complete scan): 13.33 kPa (100 mmHg) (6).

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED HYDROGEN SULFIDE (7)

Temperature, °K	Pressure		Entropy kJ/(kg•°K)		Enthalpy kJ/kg		Latent Heat of Vaporization kJ/kg	Specific Volume dm^3/kg		Density kg/dm^3	
	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
212.93	101.325	1.0	0.000 0	2.581 5	0.00	549.27	549.27	1.092 5	518.152	0.915 3	0.001 93
222.04	151.988	1.5	0.075 3	2.515 8	17.20	560.42	543.22	1.103 7	343.354	0.906 0	0.002 91
227.59	192.518	1.9	0.115 1	2.479 0	26.27	564.84	542.57	1.113 1	274.059	0.898 4	0.003 65
233.15	253.313	2.5	0.160 2	2.439 3	37.42	569.02	531.60	1.123 7	217.249	0.889 9	0.004 60
238.71	314.108	3.1	0.203 8	2.402 0	47.65	572.05	524.40	1.133 7	174.798	0.882 1	0.005 72
244.26	385.035	3.8	0.246 9	2.366 9	57.88	575.30	517.42	1.145 6	143.584	0.872 9	0.006 97
249.82	476.228	4.7	0.292 9	2.328 8	69.04	577.86	508.82	1.156 2	116.116	0.864 9	0.008 61
255.37	567.420	5.6	0.333 9	2.295 8	79.03	579.95	500.92	1.169 3	97.388	0.855 2	0.010 27
260.93	689.010	6.8	0.379 5	2.260 6	90.19	582.04	491.85	1.181 8	80.532	0.846 2	0.012 42
266.48	830.865	8.2	0.424 7	2.230 5	101.35	583.67	482.32	1.195 5	68.671	0.836 5	0.014 56
272.04	982.853	9.7	0.466 5	2.201 2	112.27	585.29	473.02	1.211 7	58.994	0.825 3	0.016 95
277.59	1 155.105	11.4	0.507 1	2.174 4	122.73	586.69	463.96	1.229 8	50.067	0.813 1	0.019 97
283.15	1 347.623	13.3	0.546 0	2.148 5	133.66	588.08	454.42	1.247 9	42.950	0.801 3	0.023 28
288.71	1 580.670	15.6	0.583 7	2.123 8	144.81	589.01	444.20	1.271 7	37.145	0.786 3	0.026 92
294.26	1 823.850	18.0	0.623 4	2.099 5	156.20	589.71	433.51	1.291 6	32.213	0.774 2	0.031 04
299.82	2 107.560	20.8	0.662 4	2.076 1	168.29	590.41	422.12	1.309 7	28.093	0.763 5	0.035 60
305.37	2 401.403	23.7	0.711 3	2.055 6	180.38	591.11	410.73	1.336 0	24.721	0.748 5	0.040 45
310.93	2 735.775	27.0	0.746 8	2.032 2	194.32	591.57	397.25	1.359 7	21.600	0.735 5	0.046 30
316.48	3 100.545	30.6	0.785 8	2.012 1	207.34	591.34	384.00	1.387 8	18.978	0.720 6	0.052 69
322.04	3 515.978	34.7	0.836 4	1.987 4	221.75	590.87	369.12	1.419 6	16.543	0.704 4	0.060 45
327.59	3 941.543	38.9	0.881 6	1.961 5	235.93	589.48	353.55	1.452 1	14.671	0.688 7	0.068 16
333.15	4 417.770	43.6	0.927 6	1.935 5	250.34	586.92	336.58	1.490 8	12.923	0.670 8	0.077 38
338.71	4 924.395	48.6	0.973 6	1.905 4	264.52	582.50	317.98	1.529 5	11.424	0.653 8	0.087 54
344.26	5 491.815	54.2	1.018 4	1.872 3	279.63	577.16	297.53	1.570 7	10.051	0.636 7	0.099 49
349.82	6 089.633	60.1	1.066 9	1.827 2	296.37	568.33	271.96	1.613 8	8.740	0.619 6	0.114 42
355.37	6 727.980	66.4	1.112 9	1.779 0	313.10	556.01	242.91	1.658 7	7.491	0.602 9	0.133 49
360.93	7 427.123	73.3	1.157 3	1.716 7	332.39	535.32	202.93	1.706 8	6.243	0.585 9	0.160 18
366.48	8 197.193	80.9									
372.04	8 926.733	88.1									
373.54	9 007.793	88.9									

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED HYDROGEN SULFIDE (7)

H, ENTHALPY, kJ/kg; **S**, ENTROPY, kJ/(kg·°K); **V**, SPECIFIC VOLUME, dm^3/kg

Pressure kPa	bar	atm		Temperature, °K 288.71	310.93	333.15	355.37	377.59	399.81	422.03	477.59	533.15	588.70
			H	626.20	645.50	667.58	689.89	711.44	735.69	759.63	818.90	879.80	941.40
101.3	1.013	1	S	2.879	2.954	2.992	3.088	3.151	3.205	3.264	3.393	3.519	3.632
			V	696.07	750.38	800.95	855.89	910.20	962.64	1 017.58	1 152.42	1 286.02	1 420.24
			H	604.35	628.30	652.01	676.41	701.52	725.92	750.59	812.16	874.45	938.14
1 010	10.1	10	S	2.268	2.364	2.443	2.510	2.577	2.636	2.694	2.824	2.946	3.059
			V	61.304	69.170	75.850	82.405	88.273	93.954	99.885	113.120	126.791	140.463
			H		609.47	634.80	659.68	684.55	711.05	737.08	801.00	866.32	931.17
2 030	20.3	20	S		2.142	2.230	2.305	2.378	2.439	2.498	2.632	2.757	2.879
			V		32.525	35.709	39.080	42.264	45.385	48.382	55.686	62.927	69.982
			H					672.69	698.73	725.23	791.94	858.65	925.59
3 040	30.4	30	S					2.251	2.314	2.378	2.515	2.648	2.766
			V					26.594	28.779	30.902	36.021	41.015	46.009
			H					657.82	684.55	712.44	781.48	850.75	919.55
4 050	40.5	40	S					2.142	2.222	2.289	2.439	2.573	2.694
			V					17.480	19.602	21.538	26.032	30.028	33.774
			H					641.55	669.21	697.80	769.39	842.14	913.50
5 070	50.7	50	S					2.050	2.138	2.213	2.377	2.519	2.640
			V					12.361	14.421	16.169	20.102	23.535	26.719
			H					618.30	649.68	679.90	754.28	828.43	902.12
6 080	60.8	60	S					1.950	2.050	2.134	2.310	2.464	2.594
			V							12.548	15.982	18.916	21.663
			H					585.99	618.53	650.84	728.48	804.26	881.20
7 090	70.9	70	S					1.854	1.966	2.059	2.255	2.414	2.544
			V							9.801	13.110	15.919	18.416

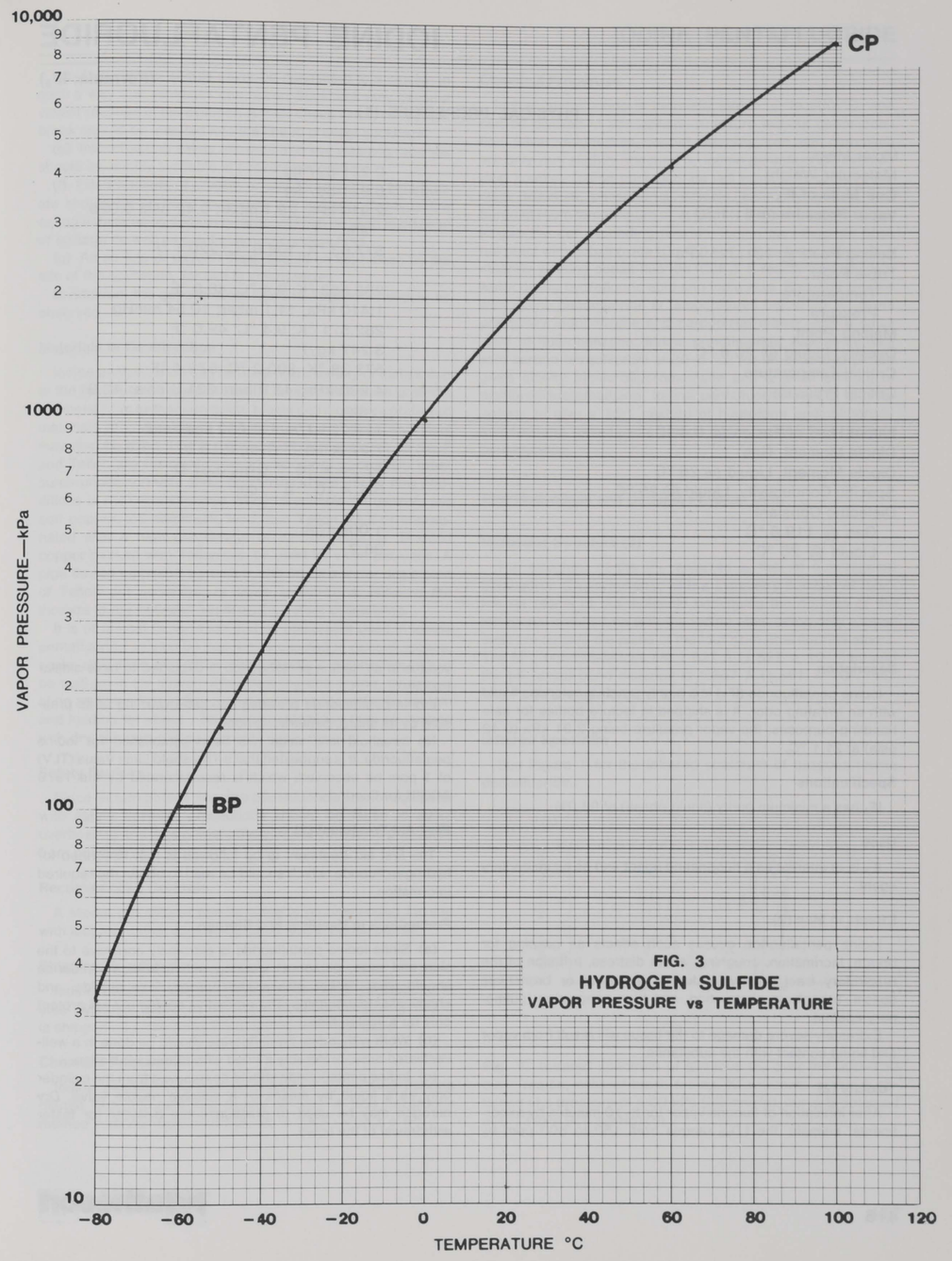


FIG. 3
HYDROGEN SULFIDE
VAPOR PRESSURE vs TEMPERATURE

IODINE PENTAFLUORIDE

(Formula: IF_5)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.221 897 kg
One Mole of IF_5	0.221 897 kg
Vapor Pressure @ 21.1 °C	2.910 kPa; 29.1 mbar; 0.42 psia 0.029 atm
Boiling Point @ 101.325 kPa	377.63 °K; 104.5 °C; 220.1 °F
Triple Point	
Temperature	282.553 °K; 9.4 °C; 48.9 °F
Pressure	1.410 kPa; 14.1 mbar; 10.54 mmHg
Melting Point	282.571 °K; 9.4 °C; 49.0 °F
Density, Liquid @ 20.6 °C	3.247 kg/l
Critical Temperature	573.38 °K; 300.2 °C; 572.4 °F
Critical Pressure	4 290 kPa; 42.9 bar; 621.6 psia; 42.3 atm
Latent Heat of Fusion @ 9.4 °C	11.222 kJ/mol; 2.682 kcal/mol
Dipole Moment, Gas	7.27×10^{-30} C·m; 2.18 D
Dipole Moment, Liquid @ 25 °C	12.24×10^{-30} C·m; 3.67 D
Specific Conductivity, Liquid @ 25 °C	$5.4 \times 10^{-6}\ \Omega^{-1}$/cm
Dielectric Constant	
Gas @ 119.6 °C	1.009 108
Liquid @ 25 °C	36.2

Description

Iodine pentafluoride (IF_5) is a highly reactive colorless liquid with an irritating odor. It is shipped in lecture bottles for safe handling purposes, the vapor pressure being 2.91 kPa (0.42 psia) at 21.1 °C.

Specifications

IF_5 has a minimum purity (liquid phase) of 98.0%.

Uses

IF_5 is of interest as a fluorinating agent and as an incendiary agent.

Effects in Man (2)

Iodine pentafluoride causes such effects as gasping for breath, lacrimation, coughing, acute distress, irritation of the respiratory tract, asphyxia due to laryngeal or bronchiole spasm, bronchiole obstruction, and lung congestion (pulmonary edema).

Extremely severe damage to the tissue will result from vapor and liquid contact with the substance.

Toxicity (2)

After inhalation of fluorine vapor for 5–10 minutes by experimental animals, the LD_{50} ranges from 150 to 800 ppm by volume in air. Iodine pentafluoride is expected to have similar toxicity.

Iodine pentafluoride provides adequate warning of its pressure by its sharp, penetrating odor.

No threshold limit value has been established for iodine pentafluoride. It is suggested that a Threshold Limit Value (TLV) of 1 ppm be observed, which is recommended by the 1979 ACGIH for fluorine.

First Aid Treatment (2)

The first aid treatment to be followed is that described for hydrogen fluoride, which should be read to obtain the required information.

Precautions in Handling and Storage

(a) Since iodine pentafluoride is extremely corrosive to the skin and eyes, personnel working with iodine pentafluoride should wear rubber gloves and aprons, face shields, and chemical safety goggles. The protective equipment will protect only for a limited time.

(b) Work with iodine pentafluoride should be done in a well-ventilated area, preferably a hood with forced ventilation.

(c) Iodine pentafluoride should be removed from the cylinder only as a liquid by means of a suitable needle valve. *Dry* nitrogen may be used to pressurize the cylinder for faster withdrawal of the liquid.

(d) The cylinder should never be connected to a system in such a way that suckback can occur. Suckback may cause a violent reaction in the cylinder. A trap, check valve, or vacuum break should be inserted into the line to prevent suckback.

(e) Instant-acting safety showers and eye washing facilities should be readily available in convenient locations.

(f) Filled buckets of cryolite or powdered sodium bicarbonate should be on hand to absorb any spillage. Dry-type fire extinguishers using sodium bicarbonate can be used to dispose of spillage as well as combat any secondary fires.

(g) An air-line or oxygen mask should be kept close by the site of the operation, for use in emergencies.

In addition, the general rules listed in Appendix I should be observed.

Materials of Construction

Iodine pentafluoride can be used with a variety of metals due to the formation of a passive metal fluoride film which protects the metal from further corrosion. Monel and nickel are preferred materials of construction; however, copper, brass, and steel may also be used. Highly fluorinated polymers such as Kel-F and Teflon are resistant to liquid and vapor at ordinary pressures under normally static conditions. Their use in flow conditions is not recommended. Material suitable for gaskets are soft copper, 2S aluminum, lead, and Teflon plain or impregnated with a high percentage of calcium fluoride. Braided copper backed with Teflon can be used for valve packings. A pipe thread lubricant, if needed, should be a water dispersion of Teflon put on in two or three applications, allowing the threads to dry between applications before assembling.

It is of utmost importance that all equipment used in iodine pentafluoride service be thoroughly cleaned to remove grease, scale, pipe dope, and other contaminants. A passive film should be built up in the system after cleaning and drying, by evacuating and bleeding iodine pentafluoride vapors into the system and holding for about 1 hour. The system can then be flushed with dry nitrogen and sealed until ready for use.

Safety Devices

Since lecture bottles of iodine pentafluoride are not equipped with safety devices, precautions should be taken to avoid overheating and thus prevent dangerous hydrostatic pressures from building up.

Recommended Controls

A Model 60L Monel needle valve is recommended for use with lecture bottles containing liquid iodine pentafluoride.

Shipping Regulations

Iodine pentafluoride is shipped under DOT regulations in steel cylinders approved for shipment of compressed gases. It is shipped as a corrosive liquid taking a "White Label".

Chemical Preparations

Iodine pentafluoride can be prepared by passing fluorine diluted with nitrogen over iodine or I_2O_5. A less hazardous method involves the use of A_gF: $3I_2 + 5A_gF \rightarrow 5A_gI + IF_5$.

Chemical Properties

Iodine pentafluoride is thermally stable up to 400 °C. and can be distilled at atmospheric pressure without decomposition. Silver, magnesium, copper, mercury, iron, and chromium are only very slightly attacked by iodine pentafluoride even on long contact. Iodine pentafluoride will react with sulfur, selenium, tellurium, phosphorus, arsenic, antimony, silicon, and boron at room temperature or at slightly elevated temperatures to give the corresponding fluoride. Iodine pentafluoride does not react with cobalt oxide (Co_3O_4) but it does react with cobalt chloride yielding cobalt fluoride (CoF_2). It reacts violently with water giving hydrofluoric acid and iodic acid. Benzene treated with iodine pentafluoride at temperatures below 50 °C. gives principally iodobenzene and carbonized matter, and a small yield of fluorobenzene. Iodine pentafluoride kept in contact with carbon tetrachloride at 30–5 °C. for an extended period gives chiefly trichlorofluoromethane and a small amount of dichlorodifluoromethane. Iodine pentafluoride reacts with iodoform to give a 15:1 mixture of fluoroform and difluorodiiodomethane. Iodine pentafluoride is less reactive than bromine pentafluoride.

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

The structure of the IF_5 molecule is that of a tetragonal octahedron (C_{4v} symmetry, with a symmetry number of four), the six atoms of the molecule occupying the corners of the tetragonal octahedron with the iodine atom being only a small distance outside the plane of the four azimuthal fluorine atoms. The I-F_{az} bond distances are 1.827 Å (1.827×10^{-10} m) and the I-F (axial) bond distance is 1.867 Å (1.867×10^{-10} m). The F_{az}-I-F_{ax} angle is 82.2 ± 0.3°.

Infrared Spectrum

See Figure 1 for the infrared spectrum of gaseous iodine pentafluoride.

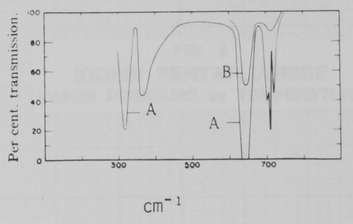


Fig. 1. Infrared spectrum of gaseous IF_5 over the 300–750 cm^{-1} region; cells of brass tubing; KI windows; curve A obtained at a pressure of 4.00 kPa (30 mmHg), curve B obtained at 0.13 kPa (<1 mmHg) (5).

IODINE PENTAFLUORIDE

Vapor Pressure (3)

The vapor pressure between 283 °K and 378 °K is represented by the equation:

$$\log_{10}p = 29.021\ 67 - 3\ 090.14/T - 6.968\ 34 \log_{10}T$$

in which p = mmHg and T = °K.

Some vapor pressures at various temperatures calculated by this equation are shown below:

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
285	1.58	15.8	11.83
295	2.89	28.9	21.68
305	5.05	50.5	37.90
315	8.46	84.6	63.48
325	13.64	136.4	102.3
335	21.24	212.4	159.3
345	32.02	320.2	240.2
355	46.90	469.0	351.7
365	66.92	669.2	501.9
377.63	101.325	1 013.25	760.0

See Figure 2 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/mol
330	39.320
377.63	36.194

Thermodynamic Properties of Iodine Pentafluoride as Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	102.876 J/(mol·°K)
Entropy, S°	334.548 J/(mol·°K)
Gibbs' Free Energy Function $(G_{298}^\circ - H_{298}^\circ)/298$	−334.548 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	20.050 kJ/mol
Enthalpy of Formation, ΔH_f°	−840.315 kJ/mol
Gibbs Free Energy of Formation, ΔG_f°	−771.659 kJ/mol

Thermodynamic Properties of Liquid Iodine Pentafluoride @ 25 °C (3)

Heat Capacity, C_p°	174.66 J/(mol·°K)
Entropy, S°	224.85 J/(mol·°K)
Gibbs Free Energy Function, $(G_{298}^\circ - H_0^\circ)/298$	−100.47 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	37.086 kJ/mol
Enthalpy of Formation, ΔH_f°	−881.99 kJ/mol
Gibbs Free Energy of Formation, ΔG_f°	−780.62 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of iodine pentafluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, 1975, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, 1977, pp. 47–51, Matheson, Lyndhurst, New Jersey.

[3] D. W. Osborne, F. Schreiner, and H. Selig, *J. Chem. Phys.* 54, 3790–3798 (1971).

[4] *JANAF Thermochemical Tables*, 2nd edition, 1971, D. R. Stull, and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[5] R. C. Lord, *et al.*, *J. Amer. Chem. Soc.* 72, 522–527 (1950).

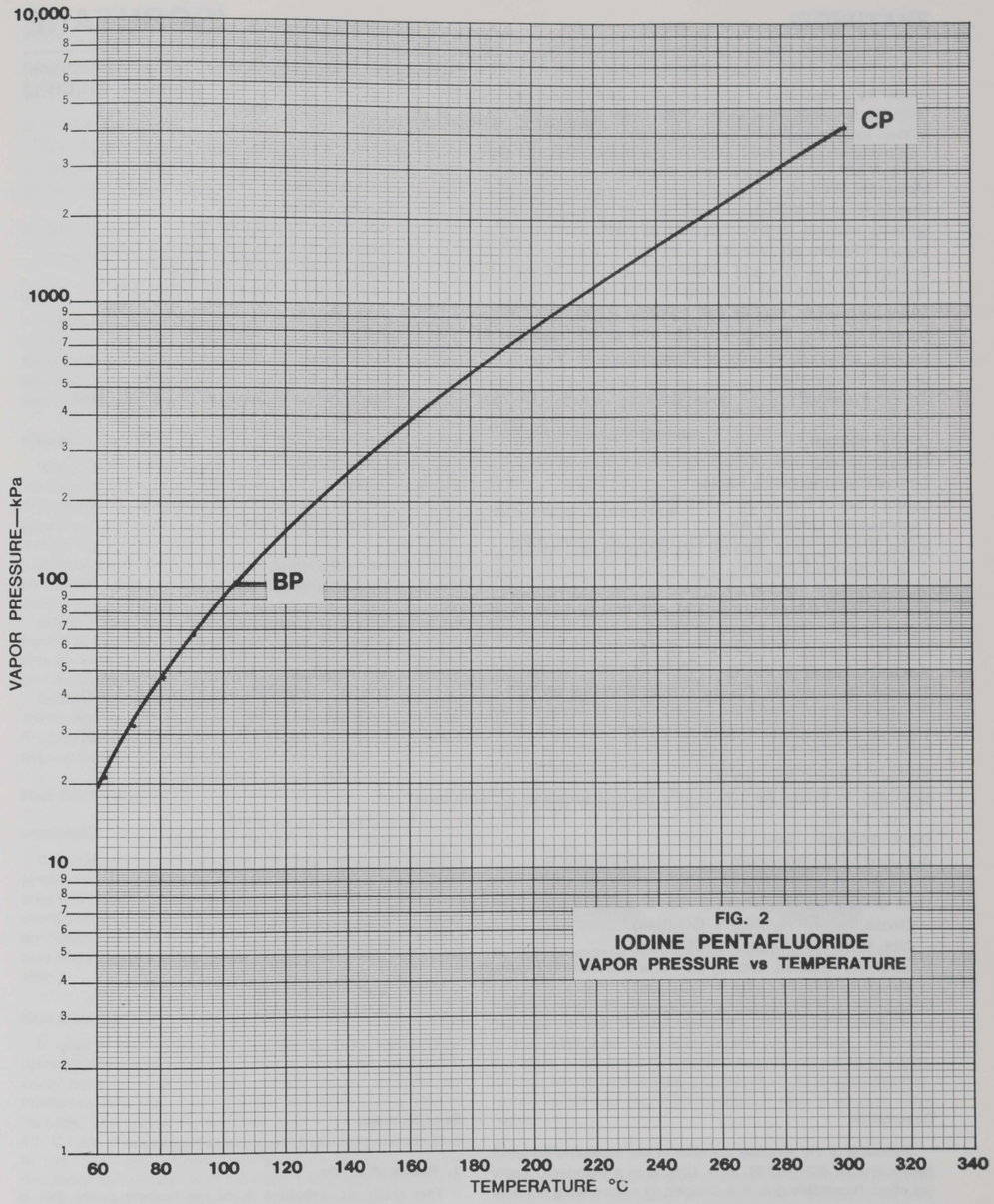


FIG. 2
IODINE PENTAFLUORIDE
VAPOR PRESSURE vs TEMPERATURE

ISOBUTANE

(Synonyms: 2-Methylpropane: Trimethylmethane)
(Formula: $CH(CH_3)_3$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.058 124 kg
One Mole of $CH(CH_3)_3$	0.058 124 kg
Specific Volume @ 21.1 °C, 101.325 kPa	405.8 dm^3/kg; 6.5 ft^3/lb
Vapor Pressure @ 21.1 °C	310 kPa; 3.1 bar; 45.4 psia; 3.1 atm
Boiling Point @ 101.325 kPa	261.42 °K; −11.7 °C; 10.9 °F
Freezing Point @ 101.325 kPa	113.55 °K; −159.6 °C; −255.3 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	2.487 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	2.064
Density, Liquid @ Saturation Pressure @ 25 °C	0.551 kg/l
Critical Temperature	408.13 °K; 135.0 °C; 275.0 °F
Critical Pressure	3 650 kPa; 36.5 bar; 529.1 psia; 36.0 atm
Critical Volume	4.525 dm^3/kg
Critical Density	0.221 kg/dm^3
Critical Compressibility Factor	0.283
Latent Heat of Fusion @ −159.6 °C	78.195 kJ/kg; 18.689 kcal/kg
Flammability Limits In Air	1.8–8.4% (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ 15.6 °C	
@ Constant Pressure	94.163 J/(mol·°K)
@ Constant Volume	85.846 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 15.6 °C, Cp/Cv	1.097
Molar Specific Heat, Liquid @ 20 °C	139.846 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.007 7 mPa·s; 0.007 7 cP
Viscosity, Liquid @ 20 °C	0.170 mPa·s; 0.170 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.017 1 W(m·°K); 41.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ 20 °C	0.094 56 W(m·°K); 226.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −20 °C	15.3 mN/m; 15.3 dyn/cm
Solubility In Water @ 102.9 kPa (partial pressure of isobutane) @ 17 °C	13 cm^3/0.1 kg water
Dipole Moment, Gas	440 × 10^{-33} C·m; 0.132 D
Autoignition Temperature	735 °K; 462 °C; 864 °F
Index of Refraction, Liquid, n_D @ −25 °C	1.350 3
Heat of Combustion, Liquid @ 25 °C and Constant Pressure	
Gross, to form H_2O(liq) + CO_2(gas)	2 848.63 kJ/mol
Net, to form H_2O(gas) + CO_2(gas)	2 628.60 kJ/mol
Heat of Combustion, Gas @ 25 °C and Constant Pressure	
Gross, to form H_2O(liq) + CO_2(gas)	2 868.72 kJ/mol
Net, to form H_2O(gas) + CO_2(gas)	2 648.68 kJ/mol

Description

Isobutane is the simplest member of the isoalkane series of hydrocarbons $(CH_3)_2CHR$, R = CH_3. It is a colorless, easily liquefied, flammable gas. It is shipped as a liquefied gas under its own vapor pressure of 210 kPa (30.4 psig) at 21.1 °C.

Specifications

Matheson supplies three grades of isobutane.

1. Research Grade

This grade of isobutane is of the highest purity that is available. A typical lot purity is 99.96 mole % as determined by freezing point. This material is furnished with a statement of analysis.

2. Instrument Grade

This grade of isobutane has a minimum purity of 99.5 mole %. Specific precautions are taken to eliminate traces of water, oil and nonvolatile matter.

3. C.P. Grade

This grade has a minimum purity of 99 mole %.

Uses

Isobutane in pure form is used for calibration work in instruments such as temperature and pressure gauges and in the filling of thermobulbs for such instruments. It is industrially important as an intermediate in the manufacture of aviation fuel and in the manufacture of many organic chemicals.

Effects in Man (2)

Isobutane has some degree of anesthetic action and is mildly irritating to the mucous membranes and/or acts as a simple asphyxiant. Thus, depending on the concentration and time of exposure, symptoms such as rapid respiration, air hunger, diminished mental alertness, muscular incoordination, faulty judgment, emotional instability, rapid fatigue, nausea, vomiting, prostration, loss of consciousness, convulsions and finally deep coma and death may occur.

ontact of the liquid form of isobutane with the skin can cause frostbite. Symptoms of frostbite are the change of skin from pink to white or grayish-yellow, pain which quickly subsides and a cold numb feeling.

Isobutane has a low order of inhalation toxicity. Thus, there are no apparent ill-effects from breathing concentrations up to 5% isobutane for 2 hours. No Threshold Limit Value (TLV) has been established for isobutane.

First Aid Treatment (2)

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration if necessary and oxygen simultaneously. Treat symptomatically thereafter.

Skin Contact

In case of skin contact with liquid isobutane, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in this armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The hazards due to the handling of isobutane stem mainly from its extreme flammability. Store and use isobutane cylinders in well-ventilated areas away from heat and all ignition sources such as flames and sparks. Never use flames to detect flammable gas leaks, use soap water solution. Do not use isobutane around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of isobutane cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all lines and equipment used with isobutane.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

All fittings and joints should be painted with soap solution to detect leaks, which will be indicated by bubble formation. Never use a flame to detect leaks.

Disposal of Leaking Cylinder

For disposal procedure see method described in Appendix II-A.

Materials of Construction

Since isobutane is a noncorrosive gas any common or commercially available metal may be used. However, piping systems or vessels to contain isobutane should be designed to have a working pressure as specified by competent engineers using a safety factor conforming to the ASME code for pressure piping.

Cylinder and Valve Description

DOT approved cylinders containing isobutane are usually of the low pressure type having a rated service pressure 1 030 kPa (150 psig). Cylinders of isobutane are equipped with valves having a standard Compressed Gas Association valve outlet No. 510 having a thread size of 0.885 inch diameter-14 threads per inch, left-hand internal threads accepting a bullet-shaped nipple. See Figure 1 for illustration of the valve outlet and mating connection. This valve outlet is standard for all liquefied petroleum gases. Valves used in this service by Matheson are of the diaphragm type and contain no packing. They are therefore relatively leak-free and require no packing adjustments. Lecture bottles have a special 5/16"-32 threads per inch, female outlet and 5/16"-18 threads per inch male dual valve outlet.

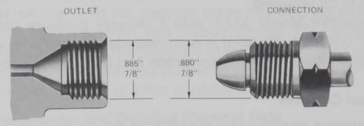


Fig. 1. CONNECTION 510 .885"-14 LH INT. accepting a Bullet Shaped Nipple

Safety Devices

A number of different safety devices are permitted on cylinders containing isobutane. A frangible disc is allowed in cylin-

ders having a minimum required test pressure of 20 680 kPa (3 000 psig) or higher, and is required in only one end of the container. A 73.9 °C (165 °F) fusible metal may be used; however, when cylinders are over 30 inches long (exclusive of the neck) this device is required in both ends. A frangible disc backed up with 73.9 °C (165 °F) fusible metal is permitted in cylinders having a minimum required test pressure of 20 680 kPa (3 000 psig) or higher, and when cylinders are over 30 inches long (exclusive of the neck) this device is at both ends. The most commonly used safety device, and that employed by Matheson, is the spring-loaded safety relief valve. If cylinder pressure becomes dangerously high, usually due to overheating, the safety relief device will open (at approximately 259 kPa) (37.5 psig) and release isobutane gas until the pressure again returns to a safe level.

Recommended Controls

Automatic Pressure Regulators

Matheson supplies single stage regulator Model 1P-510 for isobutane service. The regulator has a strong, forged brass body, brass internal parts, a neoprene diaphragm, and a neoprene seat. It has a delivery pressure range of 28–240 kPa (4–35 psig).

For accurate and sensitive low pressure control, Matheson has available a Model 70 regulator. This regulator has an oversize, pancake body of aluminum and a Buna N diaphragm. Three pressure ranges are available as follows:

Model No.	Delivery Pressure Range kPa	mbar (g)	psig
70B-510	0.5–3.0	5–30	2–12 inches water column
70-510	3.4–34.5	34–345	0.5–5.0 psig
70A-510	34.5–68.9	345–689	5–10 psig

This regulator is designed primarily for liquefied petroleum gases where it is particularly suited for fuel gas burner operation, since its steady low pressure delivery permits a stable flame to be obtained.

Regulator Model 3321, with a delivery pressure range of 28–410 kPa (4–60 psig) is recommended for use with lecture bottles containing Instrument Grade and C.P. Grade isobutane.

Manual Controls

Matheson needle valve Model 50-510 is a brass bar stock valve that is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, ¼" compression fitting, or ¼" NPT male or female pipe. It should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. A Model 31B manual needle valve can be supplied for use with lecture bottles, where accurate flow control is desired.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Isobutane is classified by the DOT as a flammable, compressed gas and is shipped with the required "Red Gas Label".

Chemical Properties (3)

Isobutane is a member of the alkane or paraffin series of hydrocarbons. The alkanes as a group are chemically inert substances, not being attacked by cold bromine, sulfuric acid, and nitric acid. However, the alkanes undergo, with a change in conditions, both chlorination and nitration and, in addition, many thermal reactions, isomerization, dehydrogenation, cyclization, and other reactions. When the alkanes are heated from 500 °C upwards, they undergo complex reactions which may be accelerated or directed by different catalysts to give a variety of products. The following reactions exemplify the different types of reactions which the alkanes undergo and which are of great importance to the petroleum industry. The reactions which may occur simultaneously are: (a) dehydrogenation, (b) isomerization, (c) thermal degradation or cracking, (d) aromatization.

(a) Dehydrogenation

This reaction is of importance in the petroleum industry for the conversion of ethane, propane, butane, isobutane, and pentanes into olefins wherein higher yields and higher reaction velocities are promoted by catalysts. Industrially the olefins so obtained are polymerized or used for alkylating isoalkanes to produce high grade motor fuel. Ethylene, propylene, and isobutylene are used for the manufacture of a great variety of industrially important aliphatic compounds.

(b) Isomerization

Normal chain alkanes containing four or more carbon atoms, or slightly branched alkanes, undergo isomerization to more highly branched alkanes with catalysts of the Friedel-Crafts type at temperature of 150–200 °C. The most effective catalyst is aluminum chloride supported on silica gel or alumina, and promoted by hydrogen chloride, but a wide variety of other catalysts and promoters may be used. Thus, isobutane and isopentane are produced from butane and pentane, respectively, and can be alkylated by propylene and butylenes to yield highly branched heptanes, octanes, and nonanes for use in aviation fuels.

(c) Thermal Degradation or Cracking

The pyrolysis of gaseous, liquid, and solid alkanes at temperatures of about 500–1000 °C has been widely studied with the object of obtaining lower branched chain alkanes and olefins. Noncatalytic pryolysis of alkanes at about 1 400–1 600 °C results in more complete degradation to yield the industrially important carbon black, hydrogen, and acetylene. By the use of suitable catalysts, the cracking temperature can be reduced to 200–500 °C, and by careful control of the conditions, the desired products can be obtained in good yields.

(d) Aromatization

The alkanes can be converted into aromatic hydrocarbons by high temperature cracking, and by hydroforming (or catalytic reforming). The aromatization of alkanes occurs at a temperature of 500–1000 °C most likely by the mechanism of first forming olefins and diolefins which combine to yield cyclic compounds. The latter in the presence of metallic catalysts are dehydrogenated into aromatic compounds. In the hydroforming process, practically quantitative conversion is effected of aliphatic hydrocarbons containing more than six carbon atoms in the chain, to yield aromatic hydrocarbons with the same number of carbon atoms. The mechanism of this reaction involves dehydrogenation of the alkane into an olefin, cyclization of the olefin to a cyclohexane derivative, and dehydrogenation of the cyclic compound to an aromatic compound.

Other Reactions of Alkanes:

(e) Oxidation

Alkanes can be oxidized by atmospheric oxygen at temperatures well below their ignition point. The rate of oxidation of the alkanes in the vapor phase increases with the length of chain and decreases by chain branching. Methyl groups have a stabilizing effect.

(f) Halogenation

The halogens, except iodine, react readily with alkanes. Little or no halogenation occurs in the dark, but in daylight or ultraviolet light methane and ethane are attacked, except by iodine, with explosive violence. Halogenation of the alkanes may be effected in the liquid or gaseous state with ultraviolet light or heat; catalysts may accelerate the reaction. The formation of isomeric halides and polysubstitution products—and, with chlorine, the danger of explosive reaction—may be minimized by control of concentrations, temperature, and catalysts, and in the case of chlorination, by carrying out the reaction in the liquid phase with carbon dioxide, nitrogen, steam, hydrogen chloride, or chlorinated hydrocarbons as diluents.

(g) Nitration

While alkanes show little or no reactivity towards nitric acid or nitrogen tetroxide at ordinary temperatures, reaction proceeds at temperatures of 100–450 °C in the liquid phase and preferably in the vapor phase to give nitroalkanes.

(h) With Inorganic Reagents

(1) Under ultraviolet light the alkanes react with a mixture of sulfur dioxide and chlorine at room temperature to give sulfonyl chlorides. (2) In the presence of organic peroxides, the alkanes react with sulfuryl chloride in the dark to yield alkyl chloride, sulfur dioxide, and hydrogen chloride. (3) Alkanes, e.g., propane, butane, and isobutane, react with sulfur dioxide in the vapor phase yielding sulfonic acids or their anhydrides, sulfones, and sulfates. (4) At about 300 °C, and above, alkanes containing four or more carbon atoms react with sulfur to give olefins, diolefins, and thiophene derivatives. (5) Alkanes, including propane, 3-methylpentane, and heptane react with phosphorus trichloride and oxygen at 25 °C to yield alkanephosphonyl chlorides which on hydrolysis give alkylphosphonic acids. (6) In the presence of aluminum chloride, alkanes react with carbon monoxide to give ketones, e.g., isobutane yields methy isopropyl ketone.

(i) With Organic Reagents

(1) In the presence of actinic light, or in the dark in the presence of organic peroxides, alkanes, e.g., pentane, heptane, and isooctane, react with oxalyl chloride or phosgene to give acid chlorides. (2) Normal alkanes react with acid chlorides in the presence of aluminum chloride to give ketones. (3) Isoalkanes condense with haloalkanes in the presence of Friedel-Crafts catalysts; e.g., 2-methyl-propane and vinyl chloride in the presence of aluminum chloride yield 1,1-dichloro-3,3-dimethylbutane. (4) Isoalkanes undergo halogen-hydrogen exchange with tertiary or secondary alkyl halides in the presence of aluminum halides. (5) Isoalkanes react with unsaturated aliphatic carboxylic acids in the presence of aluminum chloride to give saturated fatty acids. (6) Tertiary alkanes react with benzoyl peroxide yielding tert-alkyl benzoate, benzene, and carbon dioxide or (if the reaction takes this course) tert-alkyl benzene, benzyl alcohol, and carbon dioxide. (7) Tertiary alkanes and ketones in the presence of sulfuric acid react to give tert-alcohols. (8) Isoalkanes condense with aromatic hydrocarbons in the presence of silica or alumina.

Thermodynamic and Detailed Physical Data

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous isobutane.

Vapor Pressure (4)

Vapor pressures from 188.06 °K to 261.42 °K are shown below:

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
188.060	1.52	15.2	11.37
201.446	4.26	42.6	31.96

Matheson

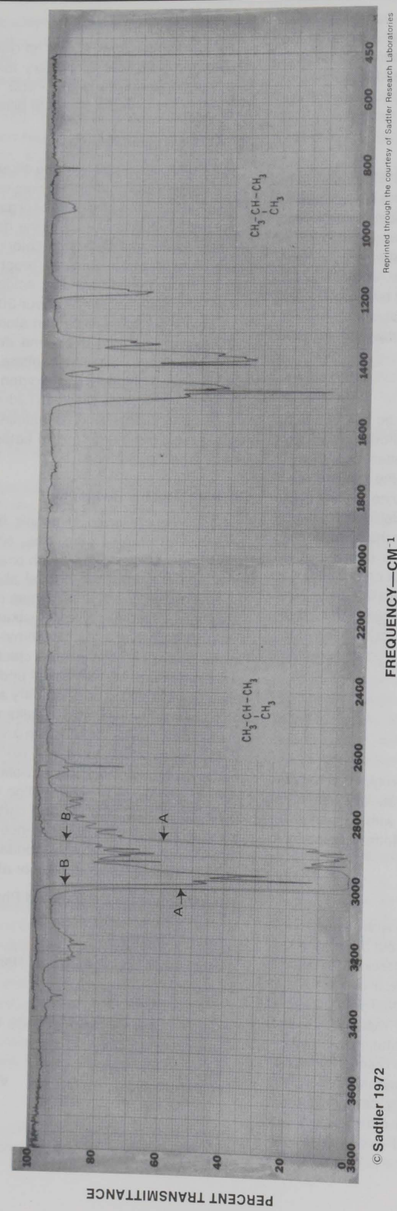


Fig. 2. Infrared spectrum of gaseous isobutane over the frequency region of 3 800 cm^{-1} to 450 cm^{-1}, 10 cm path length cell, with KBr windows; curve A (complete scan) obtained at a pressure of 6.666 kPa (50 mmHg), curve B (partial scan) at 0.667 kPa (5 mmHg) (11).

Matheson

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
216.719	11.58	115.8	86.85
229.043	23.23	232.3	174.26
245.574	52.13	521.3	391.02
251.079	66.41	664.1	498.08
254.389	76.35	763.5	572.67
259.912	95.48	954.8	716.13
261.420	101.325	1 013.25	760.00

Vapor pressure between 198.15 °K and 303.15 °K conforms to the following Antoine vapor pressure equation (5).

$$\log_{10} p = A - \frac{B}{C + t}$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.748 08, 882.80, and 240.0, respectively.

Vapor pressures from 261.42 °K to 408.13 °K are shown below (6).

Temperature, °K	Vapor Pressure kPa	bar	atm
261.42	101.3	1.013	1.0 (7)
280.65	203	2.03	2.0 (7)
312.15	507	5.07	5.0 (7)
339.95	1 010	10.1	10.0 (7)
344.26	1 110	11.1	11.00
360.93	1 570	15.7	15.52
377.59	2 160	21.6	21.29
394.26	2 890	28.9	28.56
406.87	3 580	35.8	35.32
407.77	3 630	36.3	35.85
408.13 (C.T.)	3 650	36.5	36.00

For vapor pressures at other temperatures, see Table 1 and Figure 3.

Latent Heat of Vaporization, ΔHv

Temperature, °C	ΔHv, kJ/mol
−20	21.64
−11.7	21.29
0	20.67

Thermodynamic Data

Thermodynamic properties of saturated and superheated isobutane are listed in Tables 1 and 2, respectively.

Thermodynamic Properties of Isobutane as Ideal Gas @ 25 °C (8)

Heat Capacity, C_p°	96.544 J/(mol·°K)
Entropy, S°	294.64 J/(mol·°K)
Enthalpy of Formation, ΔH_f°	−134.52 kJ/mol
Free Energy of Formation, ΔF_f°	−20.92 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of isobutane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 11–16, Matheson, Lyndhurst, New Jersey.

[3] E. H. Rodd, editor, *Chemistry of Carbon Compounds-Aliphatic Compounds, 1951*, 1A, pp. 231–243, Elsevier Publishing Co., New York, New York.

[4] V. G. Aston, R. M. Kennedy, and S. C. Schumann, *J. Amer. Chem. Soc.* 62, 2059 (1940).

[5] F. D. Rossini, *et al.*, *Selected Values of Properties of Hydrocarbons and Related Compounds*, American Petroleum Institute, Research Project 44, Carnegie Press, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

[6] J. F. Connolly, *J. Phys. Chem.* 66, 1082 (1962).

[7] *Chemical Engineers' Handbook*, 4th edition, R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, editors, *1963*, p. 3–59, McGraw-Hill Book Co., Inc., New York, New York.

[8] C. E. Miller and F. D. Rossini, *Physical Constants of Hydrocarbons, C_1 to C_{10}, 1961*, American Petroleum Institute, New York, New York.

[9] G. Hanson, *Trans. Amer. Inst. Chem. Eng.* 42, 959 (1946).

[10] B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.* 30, 673 (1938).

[11] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Matheson

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED ISOBUTANE (9)

Temperature		Pressure		Entropy* kJ/(kg·°K)		Enthalpy** kJ/kg		Latent Heat of Vaporization kJ/kg	Specific Volume dm^3/kg		Density kg/dm^3	
°K	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
244.26	−20	49.09	0.484	3.167	4.728	400.73	781.94	381.21	1.633	698.57	0.612	0.001 43
249.82	−10	62.88	0.621	3.234	4.740	412.59	789.15	376.56	1.649	555.61	0.606	0.001 80
255.37	0	79.50	0.785	3.297	4.753	424.91	796.35	371.44	1.666	446.36	0.600	0.002 24
260.93	10	99.40	0.981	3.360	4.766	437.00	803.56	366.56	1.682	362.71	0.595	0.002 76
266.48	20	122.86	1.213	3.423	4.778	449.31	810.77	361.46	1.700	297.16	0.588	0.003 37
272.04	30	150.51	1.485	3.485	4.791	462.56	818.20	355.61	1.719	245.97	0.582	0.004 07
277.59	40	182.50	1.801	3.544	4.803	475.35	825.41	350.06	1.737	204.14	0.576	0.004 90
283.15	50	220.01	2.171	3.602	4.816	488.37	832.62	344.25	1.757	171.68	0.569	0.005 83
288.71	60	262.55	2.591	3.657	4.828	500.92	839.59	338.67	1.778	145.46	0.562	0.006 88
294.26	70	310.88	3.068	3.707	4.841	513.70	846.56	332.86	1.799	123.61	0.556	0.008 09
299.82	80	365.90	3.611	3.757	4.849	526.95	853.77	326.82	1.822	105.50	0.549	0.009 48
305.37	90	427.96	4.22	3.812	4.862	540.43	860.74	320.31	1.845	90.52	0.542	0.011 05
310.93	100	497.94	4.91	3.862	4.870	554.15	867.71	313.56	1.870	78.04	0.535	0.012 81
316.48	110	575.99	5.68	3.912	4.879	568.56	874.92	306.36	1.897	67.42	0.527	0.014 83
322.04	120	663.14	6.54	3.958	4.887	583.20	881.89	298.69	1.925	58.12	0.519	0.017 21
327.59	130	759.80	7.50	4.008	4.895	597.85	888.63	290.78	1.955	50.50	0.512	0.019 80
333.15	140	866.67	8.55	4.050	4.899	612.72	895.14	282.42	1.986	44.14	0.504	0.022 66
338.71	150	983.88	9.71	4.096	4.904	627.83	901.65	273.82	2.021	38.58	0.495	0.025 92
344.26	160	1 112.12	10.98	4.138	4.908	642.71	907.69	264.98	2.057	33.90	0.486	0.029 50
349.82	170	1 252.77	12.36	4.184	4.916	657.82	913.74	255.92	2.096	29.84	0.477	0.033 51
355.37	180	1 405.84	13.87	4.226	4.916	673.62	919.54	245.92	2.140	26.28	0.467	0.038 05
360.93	190	1 571.31	15.51	4.268	4.920	689.89	925.13	235.24	2.189	23.16	0.457	0.043 18
366.48	200	1 751.26	17.28	4.310	4.920	706.63	930.01	223.38	2.243	20.35	0.446	0.049 14
372.04	210	1 946.38	19.21	4.356	4.920	724.30	934.19	209.89	2.304	17.79	0.434	0.056 21
377.59	220	2 156.67	21.28	4.406	4.920	742.89	937.91	195.02	2.379	15.48	0.420	0.064 60
383.15	230	2 383.51	23.52	4.452	4.916	762.18	940.70	178.52	2.466	13.42	0.406	0.074 52
388.71	240	2 628.27	25.94	4.502	4.912	783.10	942.33	159.23	2.572	11.55	0.389	0.086 58
394.26	250	2 891.65	28.54	4.556	4.904	805.65	942.79	137.14	2.722	9.801	0.367	0.102 03
399.82	260	3 175.02	31.34	4.615	4.891	830.76	940.47	109.71	2.934	8.053	0.341	0.124 18
405.37	270	3 485.98	34.40	4.703	4.870	865.16	932.10	66.94	3.371	6.180	0.297	0.161 81
407.93	274.6	3 640.42	35.93	4.837	4.837	911.88	911.88	0.00	4.401	4.401	0.227	0.227 22

* Entropies are referred to the ideal gas at 0 °K and 101.325 kPa^2 (1 atm) where the value is considered to be 0 kJ/(kg·°K).
** Enthalpies are referred to the saturated liquid at 273.15 °K (32 °F) where the value is considered to be 464.9 kJ/kg.

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED ISOBUTANE (10)

ENTHALPY, **H**, kJ/kg; ENTROPY, **S**, kJ/(kg·°K); SPECIFIC VOLUME, **V**, dm/kg

Pressure				Temperature, °K						
kPa	bar	atm		294.26	310.93	327.59	344.26	360.93	377.59	394.26
68.947	0.69	0.68	H	354.896	382.347	410.264	439.134	468.840	499.406	530.879
			S	1.412	1.502	1.590	1.676	1.760	1.843	1.925
			V	599.75	635.20	670.04	704.87	740.02	774.73	809.38
101.325	1.013 25	1.00	H	354.059	381.604	409.683	438.645	468.422	499.081	530.624
			S	1.355	1.446	1.534	1.620	1.705	1.788	1.869
			V	404.66	429.01	453.04	477.01	500.86	524.58	548.31
137.895	1.38	1.36	H	353.036	380.651	408.962	438.041	467.910	498.663	530.298
			S	1.309	1.400	1.489	1.575	1.660	1.743	1.825
			V	294.35	312.64	330.49	348.22	365.83	383.37	400.91
206.842	2.07	2.04	H							
			S							
			V	191.97	204.70	217.00	229.05	241.03	252.90	264.69
275.789	2.76	2.72	H	347.922	376.769	405.778	435.368	465.702	496.640	528.787
			S	1.197	1.293	1.384	1.472	1.558	1.642	1.725
			V	140.40	150.51	160.13	169.49	178.61	187.66	196.75
344.737	3.45	3.40	H							
			S							
			V		117.86	125.92	133.60	141.09	148.52	155.88
413.684	4.14	4.08	H		371.748	401.919	432.137	462.913	494.316	526.858
			S		1.232	1.318	1.408	1.496	1.581	1.665
			V		96.01	103.06	109.72	116.12	122.48	128.66
551.579	5.52	5.44	H			397.340	428.395	459.705	491.596	524.557
			S			1.268	1.360	1.449	1.536	1.621
			V			74.32	79.79	84.93	89.92	94.75
689.473	6.89	6.80	H			392.226	424.536	456.125	488.505	521.930
			S			1.224	1.320	1.410	1.499	1.585
			V			56.94	61.73	66.17	70.41	74.45
861.842	8.62	8.51	H				419.05	451.128	484.205	518.258
			S				1.275	1.369	1.459	1.547
			V				47.18	51.08	54.76	58.20
1 034.210	10.3	10.21	H				412.542	445.619	479.439	514.167
			S				1.236	1.332	1.424	1.513
			V				37.35	40.93	44.27	47.35
1 206.578	12.1	11.91	H					440.249	474.256	509.680
			S					1.298	1.392	1.483
			V					33.65	36.76	39.67
1 378.947	13.8	13.61	H					434.671	468.700	504.846
			S					1.268	1.361	1.455
			V					28.12	31.07	33.66

Table 2—*Continued*

Pressure kPa	bar	atm		Temperature, °K 294.26	310.93	327.59	344.26	360.93	377.59	394.26
1 551.315	15.5	15.31	H					428.860	462.750	499.685
			S					1.240	1.333	1.428
			V					23.69	26.54	29.04
1 723.683	17.2	17.01	H						456.404	494.200
			S						1.305	1.402
			V						22.78	25.27
1 896.052	19.0	18.71	H						449.633	488.365
			S						1.277	1.377
			V						19.60	22.11
2 068.420	20.07	20.41	H						443.271	482.322
			S						1.255	1.352
			V						16.83	19.42
2 413.157	24.1	23.82	H							467.910
			S							1.302
			V							15.08
2 757.893	27.6	27.22	H							447.688
			S							1.240
			V							11.67

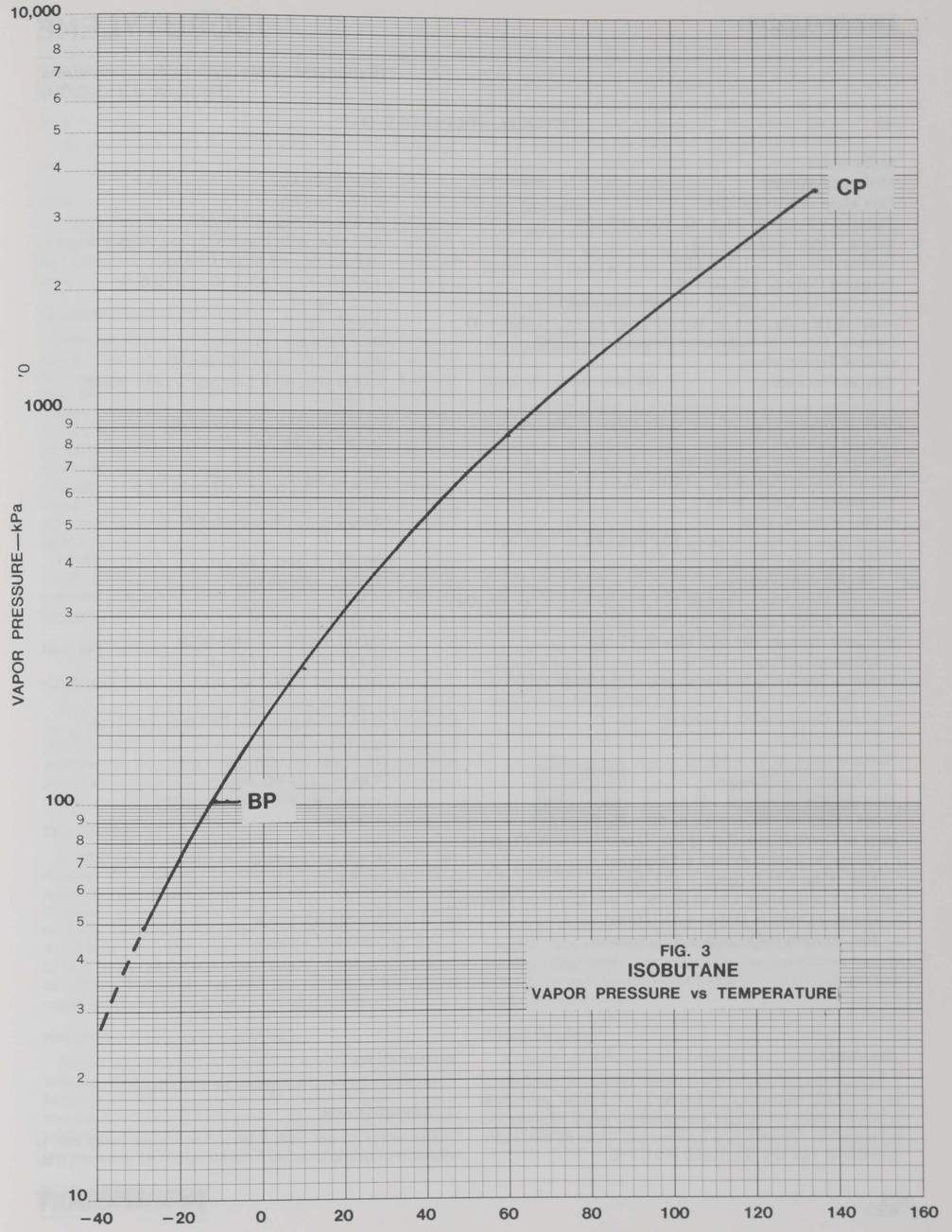


FIG. 3
ISOBUTANE
VAPOR PRESSURE vs TEMPERATURE

ISOBUTYLENE

(Synonyms: 2-Methylpropene; Isobutene)
(Formula: $(CH_3)_2C{:}CH_2$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.056 108 kg
One Mole of $(CH_3)_2C{:}CH_2$	0.056 108 kg
Specific Volume @ 21.1 °C, 101.325 kPa	418.2 dm^3/kg; 6.7 ft^3/lb
Vapor Pressure @ 21.1 °C	269 kPa; 2.69 bar; 39.0 psia; 2.65 atm
Boiling Point @ 101.325 kPa	266.25 °K; −6.9 °C; 19.6 °F
Freezing Point @ 101.325 kPa	132.80 °K; −140.4 °C; −220.6 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	2.307 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.947
Density, Liquid @ Saturation Pressure @ 25 °C	0.587 9 kg/l
Critical Temperature	417.88 °K; 144.7 °C; 292.5 °F
Critical Pressure	4 000 kPa; 40.0 bar; 580.2 psia; 39.48 atm
Critical Volume	4.274 dm^3/kg
Critical Density	0.234 kg/dm^3
Critical Compressibility Factor	0.275
Latent Heat of Fusion @ −140.4 °C	105.71 kJ/kg; 25.265 kcal/kg
Flammability Limits In Air	1.8–8.8% (by volume)
Dipole Moment, Gas	1.668×10^{-30} C·m; 0.5 D
Molar Specific Heat, Gas @ 101.325 kPa @ 15.6 °C	
@ Constant Pressure	86.883 J/(mol·°K)
@ Constant Volume	78.573 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa 15.6 °C, Cp/Cv	1.106
Specific Heat, Liquid @ −10 °C	2.176 kJ/(kg·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.008 3 mPa.s; 0.008 3 cP
Viscosity, Liquid @ −10 °C	0.175 mPa·s; 0.175 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.016 94 W(m·°K); 40.5×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −10 °C	0.113 8 W/(m·°K); 272.0×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −10 °C	16.1 mN·m; 16.1 dyn/cm
Autoignition Temperature	738 °K; 465 °C; 869 °F
Flash Point	< 266 °K; < −7 °C; < 20 °F
Index of Refraction, Liquid, n_D @ −25 °C	1.392 6
Heat of Combustion, Gas @ 25 °C and Constant Pressure	
Gross, to form H_2O (liq) + CO_2 (gas)	2 700.48 kJ/mol
Net, to form H_2O (gas) + CO_2 (gas)	2 524.26 kJ/mol
Heat of Combustion, Liquid @ 25 °C and Constant Pressure	
Gross, to form H_2O (liq) + CO_2 (gas)	2 679.89 kJ/mol
Net, to form H_2O (gas) + CO_2 (gas)	2 503.87 kJ/mol

Description

At room temperature and atmospheric pressure, isobutylene is a colorless, flammable gas having an unpleasant odor which is similar to that of coal gas. Isobutylene is easily liquefied and is shipped in cylinders as a liquefied gas under its own vapor pressure of 168 kPa (24.3 psig) at 21.1 °C.

Specifications

Matheson supplies two grades of isobutylene.

1. Research Grade

This grade of isobutylene is of the highest purity that is available. A typical lot purity is 99.52 mole % as determined by freezing point. This material is furnished with a statement of purity.

2. C.P. Grade

This grade of isobutylene has a minimum purity of 99 mole %.

Uses

Isobutylene is used in organic synthesis and in the production of high octane aviation gasoline. Its main use is in the production of Butyl rubber where it comprises 98% of the raw material used.

Effects in Man and Toxicity (2)

Isobutylene has some degree of anesthetic action and is mildly irritating to the mucous membranes and/or acts as a simple asphyxiant. Thus, depending on the concentration and time of exposure, symptoms such as rapid respiration, air hunger, diminished mental alertness, muscular incoordination, faulty judgement, emotional instability, rapid fatigue, nausea, vomiting, prostration and loss of consciousness, convulsions and finally deep coma and death may occur.

Contact of the liquid form of isobutylene with the skin can cause frostbite. Symptoms of frostbite are the change of skin from pink to white or grayish-yellow, pain which quickly subsides and cold and numb feelings.

Isobutylene is about 4.5 times as toxic as ethylene. Athough no Threshold Limit Value (TLV) has been established for isobutylene, a maximum permissible limit of 4 000 ppm has been suggested for workroom atmospheres.

First Aid Treatment (2)

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration and oxygen simultaneously. Treat symptomatically thereafter.

Skin Contact

In case of skin contact with liquid isobutylene, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The hazards due to the handling of isobutylene stem mainly from its extreme flammability. Store and use isobutylene cylinders in well-ventilated areas away from heat and all ignition sources such as flames and sparks. Never use flames to detect flammable gas leaks, use soap water solution. Do not use isobutylene around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of isobutylene cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all lines and equipment used with isobutylene. The above general rules should apply in the handling and storage of isobutylene.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

All fittings and joints should be painted with soap solution to detect leaks, which will be indicated by bubble formation. Never use a flame to detect leaks.

Disposal of Leaking Cylinders

For disposal see Appendix II-A. Alternatively, the gas can be absorbed in concentrated sulfuric acid.

Materials of Construction

Since isobutylene is a noncorrosive gas any common or commercially available metal may be used. However, piping systems or vessels to contain isobutylene should be designed to have a working pressure as specified by competent engineers using a safety factor conforming to the ASME code for pressure piping.

Cylinder and Valve Description

DOT approved cylinders containing isobutylene are usually of the low pressure type having a rated service pressure of 1 034 kPa (150 psig) or more. Cylinders of isobutylene are equipped with valves having Compressed Gas Association (CGA) valve outlet No. 510 having thread size of 0.885 inch diameter-14 threads per inch, left-hand internal threads accepting a bullet-shaped nipple. See Figure 1 for illustration of the valve outlet and mating connection. This valve outlet is standard for all liquefied petroleum gases. Valves used in this service by Matheson are of the diaphragm type and contain no packing. They are therefore relatively leak-free and require no packing adjustments. Lecture bottles have a special 5/16"-32 threads per inch, female outlet and a 9/16"-18 threads per inch male dual valve outlet.

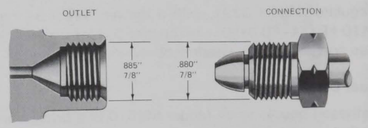


Fig. 1. CONNECTION 510 .885"-14 LH INT. accepting a Bullet Shaped Nipple

Safety Devices

A number of different safety devices are permitted on cylinders containing isobutylene. A frangible disc is allowed in cylinders having a minimum required test pressure of 20 680 kPa (3 000 psig) or higher, and is required in only one end of the container. A 73.9 °C (165 °F) fusible metal may be used; however, when cylinders are over 30 inches long (exclusive of

the neck) this device is required in both ends. A frangible disc backed up with 73.9 °C (165 °F) fusible metal is permitted in cylinders having a minimum required test pressure of 20 680 kPa (3 000 psig) or higher and when cylinders are over 30 inches long (exclusive of the neck) this device is required at both ends. The most commonly used safety device, which is employed by Matheson, is the spring-loaded safety relief valve. If cylinder pressure becomes dangerously high, usually due to overheating, the safety relief device will open (at approximately 2 590 kPa (375 psig) and release isobutylene gas until the pressure again returns to a safe level.

Recommended Controls

Automatic Pressure Regulators

Matheson supplies a single stage regulator designated as Model 1P-510 for use with isobutylene. This regulator will deliver from 28–240 kPa (4–35 psig). It is equipped with delivery pressure gauge and needle valve for accurate flow control. No tank gauge is supplied since the vapor pressure of the gas over liquid isobutylene will remain constant as long as any liquid remains in the cylinder; therefore, the pressure is no indication of cylinder content. A tank gauge, however is available.

For low pressure regulation, Matheson supplies a Model 70 regulator constructed of a forged aluminum body and Buna N diaphragm. This regulator is constructed with an oversize, pancake body to allow sensitive and accurate low pressure control. Three pressure ranges are available as follows:

Model No.	Delivery Pressure kPa	mbar (g)	psig
70B-510	0.5–3.0	5–30	2–12 inches water column
70-510	3.4–34.5	34–345	0.5–5.0 psig
70A	34.5–68.9	345–689	5–10 psig

Regulator Model 3321, with a delivery pressure range of 28–410 kPa (4–60 psig) is recommended for use with lecture bottles containing C.P. Grade isobutylene.

Manual Controls

Matheson needle valve Model 50-510 is a brass bar stock valve that is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, ¼″ compression fitting, or ¼″ NPT male or female pipe. It should be used only where manual flow control is needed and should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. A Model 31B manual needle valve can be supplied for use with lecture bottles, where accurate flow control is desired.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Isobutylene is classified by the DOT as a flammable, compressed gas and is shipped with the required "Red Gas Label".

Chemical Properties

Isobutylene undergoes the typical reactions of olefins or the alkene series of hydrocarbons.

Some of the general reactions of alkenes are as follows:

(a) The alkenes combine with hydrogen halides forming alkyl halides, the descending order of reactivity being HI, HBr, HCl. Normal addition follows Markownikoff's rule, the halogen atom becoming attached to the carbon carrying the fewest hydrogen atoms. Peroxides reverse the direction of addition of hydrogen halides to alkenes.

(b) The alkenes combine with halogens: the order of decreasing addition rate being chlorine, bromine, iodine. At higher temperatures, substitution on the carbon adjacent to the doubly bonded carbon atoms can occur.

(c) The alkenes are hydrogenated to the corresponding alkanes in the presence of suitable catalysts (platinum, palladium, Raney nickel).

(d) The alkenes combine with concentrated sulfuric acid forming alkyl hydrogen sulfates which on hydrolysis yield alcohols. The method is a convenient one for the hydration of double bonds.

(e) With positive halogen compounds, like *N*-bromosuccinimide, the alkenes are halogenated at the alpha carbon—allylic halogenation.

(f) With hypochlorous acid, the alkenes give chlorohydrins.

(g) In the presence of aluminum chloride, the alkenes combine with acyl halides giving halogeno ketones.

(h) The alkenes combine with carbon monoxide and hydrogen in the presence of cobalt under high pressure to form aldehydes.

(i) The alkenes are readily oxidized by a variety of oxidizing agents, e.g., potassium permanganate, hydrogen peroxide, perbenzoic acid, etc.

(j) The alkenes can be polymerized to polyalkenes under suitable conditions, the polymerization being catalyzed by aluminum chloride or boron trifluoride.

(k) At elevated temperatures and pressures, and in the presence of sulfuric acid or other catalysts, alkanes may add to alkenes.

(l) The alkenes may be isomerized by heating alone or in the presence of catalysts.

Thermodynamic and Detailed Physical Data

Molecular Structure

Isobutylene has C_{2v} symmetry, and the total symmetry number is 18.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous isobutylene.

Vapor Pressure

The vapor pressure of isobutylene up to its boiling point is shown below (3).

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
168.05	0.133	1.33	1
176.65	0.667	6.67	5
191.25	1.33	13.3	10
199.75	2.67	26.7	20
209.35	5.33	53.3	40
215.45	8.00	80.0	60
223.85	13.33	133.3	100
236.45	26.66	266.6	200
250.95	53.33	533.3	400
266.25 (B.P.)	101.325	1 013.25	760

The vapor pressure of isobutylene between 205.15 °K and 312.15 °K is expressed by the following Antoine vapor pressure equation (4):

$$\log_{10} p = A - \frac{B}{C + t}$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.841 34, 923.2, and 240.0, respectively.

For additional vapor pressure values, see Table 1 and Figure 3.

Vapor pressure values for isobutylene above 101.325 kPa (1 atm) are shown below (5).

Temperature, °K	Vapor Pressure kPa	bar	atm
266.25	101.325	1.013 25	1.000
285.42	202.650	2.03	2.000
303.15	348.963	3.49	3.444
323.15	605.518	6.06	5.976
348.15	1 100.39	11.0	10.86
373.15	1 831.96	18.3	18.08
398.15	2 878.64	28.8	28.41
417.88 (C.T.)	4 000.31	40.0 (C.P.)	39.48

For additional vapor pressure values, see Figure 3.

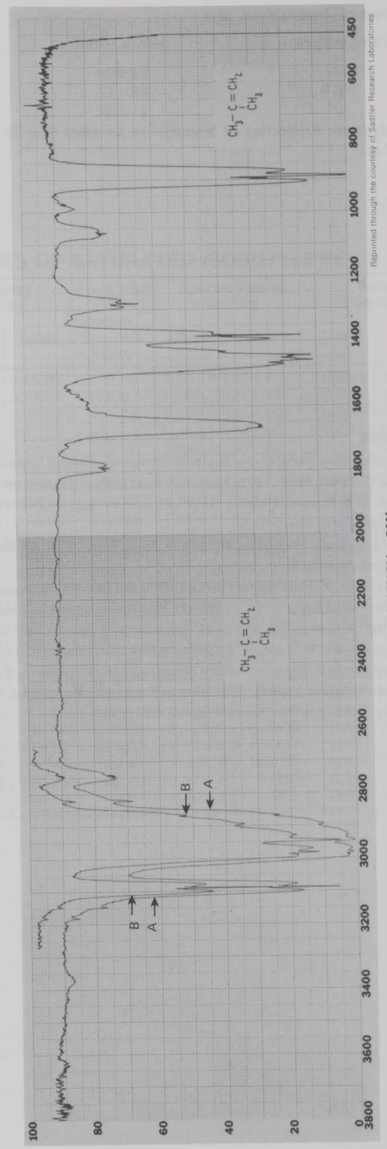


Fig. 2. Infrared spectrum of gaseous isobutylene in the frequency region of 3 800 cm^{-1} to 450 cm^{-1}; 10 cm. path-length cell with KBr windows; curve A (complete scan) obtained at a pressure of 5.333 kPa (40 mmHg), curve B (partial scan) at 1.067 kPa (8 mmHg) (8).

Latent Heat of Vaporization, ΔHv

Temperature	ΔHv, kJ/mol
−20	22.983
−6.9	22.117
0	21.832

Thermodynamic Properties of Isobutylene As Ideal Gas @ 25 °C (6)

Heat Capacity, C_p°	89.12 J/(mol·°K)
Entropy, S°	293.59 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_0^\circ)/298$	−236.27 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	17.079 kJ/mol
Enthalpy of Formation, ΔH_f° (7)	−16.903 kJ/mol
Free Energy of Formation, ΔF_f° (7)	58.074 kJ/kg

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of isobutylene, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases-First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 11-16, Matheson, Lyndhurst, New Jersey.

[3] *Chemical Engineers' Handbook*, 4th edition, R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, editors, *1963*, p. 3-55, McGraw-Hill Book Co., Inc., New York, New York.

[4] *Selected Values of Properties of Hydrocarbons and Related Compounds*, Research Project 44, American Petroleum Institute, Carnegie Press, Carnegie Institute of Technology, Pittsburgh, Pennsylvania (now at Texas A & M University, College Station, Texas).

[5] J. A. Beattie, H. C. Ingersoll, and W. H. Stockmayer, *J. Amer. Chem. Soc.* 64, 546 (1942).

[6] J. E. Kilpatrick, and K. S. Pitzer, *J. Research Natl. Bur. Stand.* 37, 163-171 (1946).

[7] C. E. Miller and F. D. Rossini, *Physical Properties of Hydrocarbons, C_1 to C_{10}*, July *1961*, American Petroleum Institute, New York, New York.

[8] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[9] G. Hanson, *Trans, Am. Inst. Chem. Eng.* 42, 959 (1946).

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED ISOBUTYLENE (9)

Temperature		Pressure		Entropy kJ/(kg·°K)		Enthalpy kJ/kg		Latent Heat of Vaporization, ΔHv kJ/kg	Specific Volume dm³/kg		Density kg/dm³	
°K	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
244.26	−20	39.231	0.387	3.243	4.933	402.36	815.65	413.29	1.537 6	907.70	0.650	0.001 10
249.82	−10	50.745	0.501	3.310	4.945	414.22	822.85	408.63	1.552 0	715.42	0.644	0.001 40
255.37	0	64.811	0.640	3.376	4.954	426.30	830.06	403.76	1.566 9	568.09	0.638	0.001 76
260.93	10	81.909	0.808	3.439	4.966	438.39	837.03	398.64	1.582 6	456.97	0.632	0.002 19
266.48	20	102.249	1.009	3.502	4.979	450.48	844.24	393.76	1.598 2	372.07	0.626	0.002 69
272.04	30	126.38	1.247	3.556	4.987	462.56	851.44	388.88	1.615 0	305.27	0.619	0.003 28
277.59	40	154.65	1.526	3.611	4.996	474.65	858.65	384.00	1.631 9	253.46	0.613	0.003 95
283.15	50	187.67	1.852	3.669	5.008	487.20	865.62	378.42	1.649 3	211.63	0.606	0.004 73
288.71	60	225.73	2.228	3.724	5.017	499.76	872.60	372.84	1.668 1	177.92	0.599	0.005 62
294.26	70	269.24	2.657	3.778	5.025	512.54	879.57	367.03	1.686 8	150.45	0.593	0.005 65
299.82	80	318.88	3.147	3.828	5.033	525.56	886.54	360.98	1.707 4	127.98	0.586	0.007 81
305.37	90	375.21	3.703	3.879	5.042	538.57	893.52	354.95	1.728 0	109.87	0.579	0.009 10
310.93	100	438.78	4.330	3.929	5.050	551.59	900.49	348.90	1.749 9	94.27	0.571	0.010 61
316.48	110	510.14	5.03	3.975	5.054	565.07	907.46	342.39	1.773 0	81.16	0.564	0.012 32
322.04	120	590.05	5.82	4.021	5.063	578.55	913.97	335.42	1.797 9	70.54	0.556	0.014 18
327.59	130	678.99	6.70	4.067	5.067	592.73	920.48	327.75	1.823 5	61.179	0.548	0.016 35
333.15	140	777.73	7.68	4.113	5.071	607.38	926.99	319.61	1.851 0	53.251	0.540	0.018 78
338.71	150	886.66	8.75	4.159	5.075	622.49	933.03	310.54	1.879 7	46.446	0.532	0.021 53
349.82	170	1 138.32	11.23	4.247	5.084	652.24	944.89	292.65	1.945 9	35.709	0.514	0.028 00
360.93	190	1 438.93	14.20	4.326	5.084	682.69	955.81	273.12	2.025 8	27.718	0.494	0.036 08
372.04	210	1 793.32	17.70	4.410	5.084	715.46	966.04	250.58	2.122 6	21.600	0.471	0.046 30
383.15	230	2 208.38	21.80	4.494	5.079	750.79	974.87	224.08	2.239 3	16.731	0.447	0.059 77
394.26	250	2 691.70	26.57	4.586	5.067	790.54	980.45	189.91	2.403 5	12.735	0.416	0.078 52
405.37	270	3 250.18	32.08	4.699	5.050	834.24	976.73	142.49	2.684 4	9.052	0.373	0.110 47
417.87	292.5	4 000.32	39.48	4.971	4.971	940.47	940.47	0.0	4.251 3	4.251 3	0.235	0.235 22

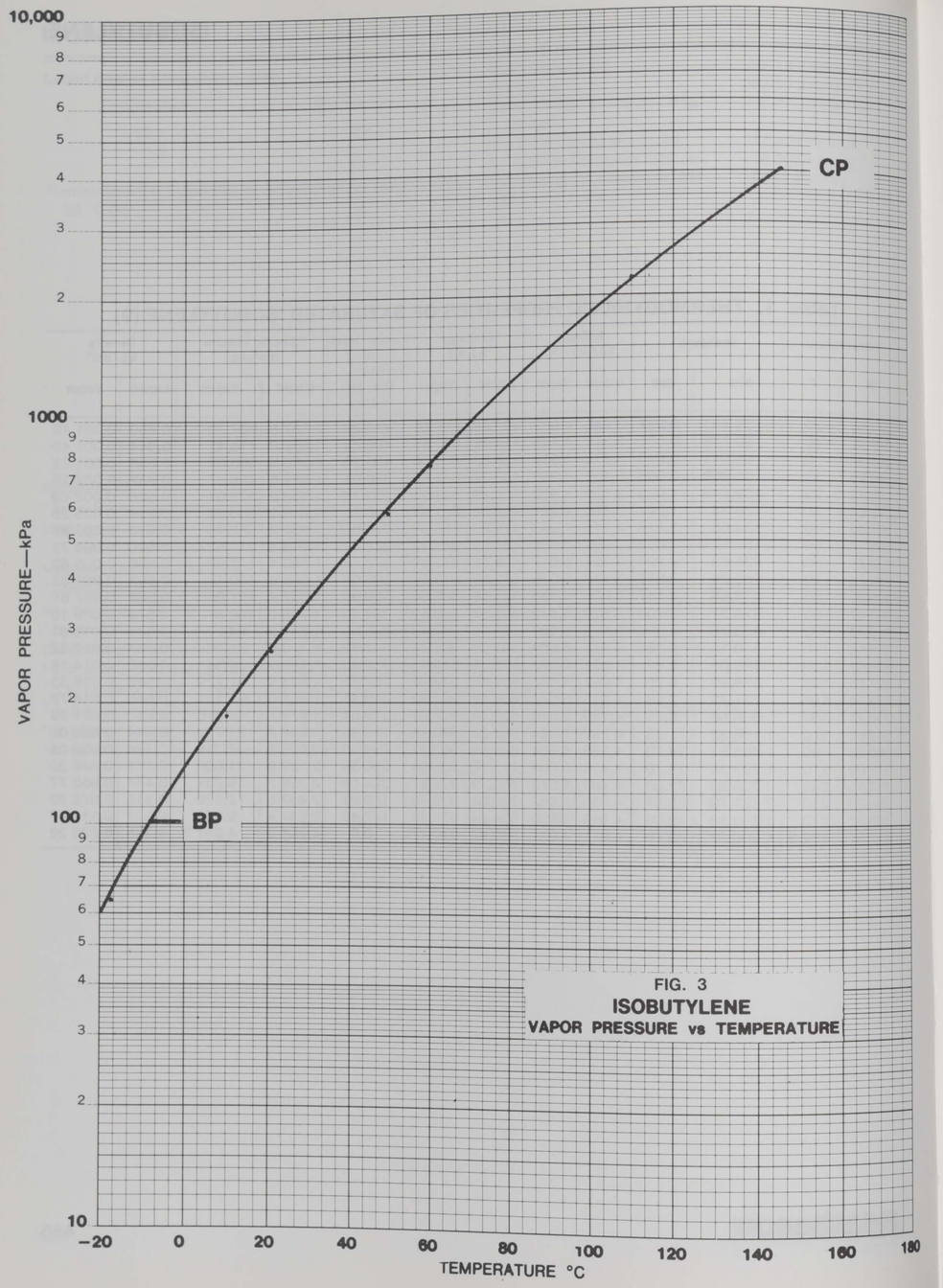


FIG. 3
ISOBUTYLENE
VAPOR PRESSURE vs TEMPERATURE

KRYPTON

(Formula: Kr)

PHYSICAL PROPERTIES (1)

Atomic Mass	
Atomic Weight	0.083 80 kg
One Mole of Kr	0.083 80 kg
Specific Volume @ 21.1 °C, 101.325 kPa	287.8 dm^3/kg; 4.61 ft^3/lb
Boiling Point @ 101.325 kPa	119.80 °K; −153.4 °C; −244.0 °F
Triple Point	
Temperature	115.77 °K; −157.4 °C; −251.3 °F
Pressure	73.15 kPa; 731.5 mbar; 10.6 psia; 548.7 mmHg
Absolute Density, Gas @ 101.325 kPa @ 25 °C	3.427 4 kg/cm^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	2.89
Density, Liquid @ Saturation Pressure @ −153.2 °C	2.412 kg/l
Critical Temperature	209.40 °K; −63.8 °C; −82.8 °F
Critical Pressure	5 490 kPa; 54.9 bar; 796.5 psia; 54.2 atm
Critical Volume	1.100 7 dm^3/kg
Critical Density	0.908 5 kg/dm^3
Critical Compressibility Factor	0.291
Latent Heat of Fusion @ −157.4 °C	19.572 kJ/kg; 4.678 kcal/kg
Dipole Moment Gas	0 C·m
Molar Specific Heat @ 101.325 kPa @ 25 °C	
@ Constant Pressure	21.037 J/(mol·°K)
@ Constant Volume	12.622 J/(mol.·K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.667
Viscosity, Gas @ 101.325 kPa @ 15.2 °C	0.024 36 mPa·s; 0.024 36 cP
Viscosity, Liquid @ −153.4 °C	0.431 mPa·s; 0.431 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 20 °C	0.009 29 W(m·°K) 22.2 × 10^{-6} cal·cm/(s·cm^3·°C)
Thermal Conductivity, Liquid @ −153.4 °C	0.088 28 W(m·°K); 211.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Solubility In Water @ 101.325 kPa (partial pressure of krypton) @ 20 °C	59.4 cm^3 Kr/1 kg water
Dielectric Constant, Gas @ 0 °C, 101.325 kPa	1.000 768
Velocity of Sound in Gaseous Kr	213 m/s
First Ionization Potential	224.28 × 10^{-18} J; 14.0 eV
Refractive Index, Gas @ 101.325 kPa, n_D @ 25 °C	1.000 391 2

Description

Krypton is a member of Group VIII A elements in the periodic system. It is a colorless, odorless, and tasteless gas. It exists in very minute traces in the atmosphere (1.14 ppm by volume).

Krypton is shipped in small cylinders at various pressures which range from 1 520 kPa (220 psig) to 7 240 kPa (1 050 psig) depending on the cylinder size, and in glass 1 liter flasks.

Specifications

Krypton is supplied by Matheson in an extremely pure Research Purity Grade only; minimum purity is 99.995%.

Uses

Krypton has some use in the lighting and electronic industry. A radioactive isotope of krypton, Kr^{85}, is widely used in the medical field in heart shunt studies, and as a triggering agent in discharge type electronic tubes.

Effects in Man and Toxicity (2)

Krypton is nonflammable and nontoxic but it can act as a simple asphyxiant by diluting the air inspired to such an extent that an oxygen deficiency results.

The coordinating capacity of the nervous system is impaired

by even slight degrees of oxygen deficiency; the subject can not think clearly or control his limbs accurately. The development of symptoms depends on the degree and duration of the oxygen deficiency and also on the rapidity with which the deficiency is developed. In sudden and acute asphyxia, unconsciousness is immediate. When the asphyxia develops slowly enough the following symptoms appear: increased volume of breathing, accelerated pulse rate, muscular incoordination, faulty judgment, emotional instability, fatigue, fainting, nausea, vomiting, bewilderment and respiration in gasps.

No Threshold Limit Values (TLV) have been established for krypton.

First Aid Treatment (2)

If the subject is conscious and becomes aware of symptoms of asphyxia, he should go to an uncontaminated area and inhale fresh air or oxygen.

An unconscious subject must be carried to an uncontaminated area and given artificial respiration with simultaneous administration of oxygen as promptly as possible.

Few, even those who have been severely asphyxiated, fail to make complete recoveries after receiving oxygen inhalation. Treat symptomatically thereafter.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Materials of Construction

Since krypton is inert no special materials of construction are required. However, any piping or vessels containing krypton should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

Krypton is packaged in DOT approved steel cylinders. The standard valve outlet accepted by the Compressed Gas Association (CGA) and the one used by Matheson is designated as valve outlet connection No. 580. It has a 0.965 inch diameter right-hand internal threads accepting a bullet-shaped nipple (see Figure 1 for illustration).

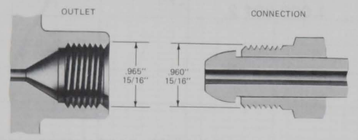


Fig. 1. **CONNECTION 580** .965"-14 RH INT. accepting a Bullet Shaped Nipple

Safety Devices

Cylinders containing krypton have safety devices of either the frangible disc type or frangible disc backed up with fusible metal, melting at approximately 100 °C (212 °F). These safety devices are usually an integral part of the cylinder valve, situated opposite the valve outlet.

Recommended Controls

Single stage regulators Model 19-580 and Model 3500-580 with metal diaphragms are recommended for use with krypton. The delivery pressure ranges of these regulators are 28–345 kPa (4–50 psig) and 28–520 kPa (4–75 psig), respectively.

The Model 19-580 regulator is recommended for applications requiring low diffusion and leakage rates. It is of all brass construction. The delivery pressure range is 28–345 kPa (4–50 psig). An optimal helium leak rate certification is available with this regulator. The maximum acceptable helium leak rate is 2×10^{-9} cm^3 per second inboard.

The Model 3500 is especially designed for high purity systems requiring all stainless steel construction. This regulator has a body of type 316 stainless steel, a diaphragm of 316 stainless steel, a Tefzel seat, and Teflon gaskets. An optimal helium leak rate certification may be obtained. The maximum helium leak rate is 2×10^{-10} cm^3 per second inboard.

The following two stage regulators are recommended for high purity applications of krypton: Model 3800-580 and Model 3104-580.

The Model 3800 regulator has a type 316 stainless steel body, a type 316 stainless steel diaphragm, a Tefzel seat, and Kel-F and Teflon gaskets. It has a delivery pressure range of 28–620 kPa (4–90 psig).

The Model 3104 regulator has a brass body, a type 302 stainless steel diaphragm, a Kel-F seat, Teflon and Nylon gaskets, and a Teflon relief valve seat. The delivery pressure range of this regulator is 28–690 kPa (4–100 psig).

Optimal helium leak rate certifications may be obtained with these regulators. The maximum acceptable helium leak rate for these two regulators is 2×10^{-9} cm^3 per second inboard.

Manual Controls

A Model 4351-580 manual needle valve is available for direct attachment to the cylinder valve outlet. This type of control is used mainly where intermittent flows are necessary, or where it is desired to control the flow of gas directly from the cylinder. This type of needle valve will allow control of extremely slow flow rates on up to relatively large flow rates. However, pressure cannot be controlled with such a valve, and dangerous pressures can build up if a line or system becomes plugged.

Flowmeters

Matheson Series 7600 laboratory brass or stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass or stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Matheson

Shipping Regulations

Krypton is shipped in high pressure steel cylinders as a nonflammable compressed gas, taking a DOT "Green Label".

Commercial Preparation

Krypton is available only from the atmosphere and is obtained by the liquefaction and fractionation of large quantities of air.

Chemical Properties

Krypton is chemically inert under all normal conditions, and does not combine chemically with other elements or compounds. However, KrF_2 is formed when a mixture of Krypton and fluorine is subjected to an electric discharge at 84 °K or irradiated with an electron beam at 123 °K.

KrF_2 is not very stable, decomposing rapidly at 0 °C. KrF_4 has been prepared as an unstable colorless solid by subjecting the elements to an electric discharge at low temperatures.

Thermodynamic and Detailed Physical Data

Atomic Structure

The krypton atom has a valence shell of 8 electrons, which is a closed octet. This closed-shell structure is extremely stable and results in krypton being relatively inert chemically. Krypton has an atomic radius of 2.00×10^{-10} m (2.00 Å).

Vapor Pressure

The vapor pressure of liquid krypton from 112.05 °K to 129.23 °K corresponds to the following Antoine vapor pressure equation (3):

$$\log_{10} p = A - \frac{B}{C + t} \quad \text{or} \quad t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.630 70, 416.38, and 264.45, respectively.

Some calculated vapor pressures are shown below:

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
112.05	53.329	533.3	400
114.60	66.661	666.6	500
116.78	79.993	799.9	600
118.69	93.326	933.3	700
119.05	95.992	959.9	720
119.40	98.659	986.6	740
119.57	101.325	1 013.25	760
120.07	103.991	1 040	780
120.40	106.658	1 067	800
121.96	119.990	1 200	900
123.38	133.322	1 333	1 000
125.94	159.987	1 600	1 200
129.23	199.984	2 000	1 500

Vapor pressures from the boiling point up to the critical point are shown below (4).

Temperature, °K	Vapor Pressure kPa	bar	atm
119.57 (B.P.)	101.325	1.013	1 (3)
129.30	202.650	2.03	2 (3)
143.15	506.625	5.07	5
155.15	1 013.250	10.1	10
171.45	2 026.500	20.3	20
184.35	3 039.750	30.4	30
194.75	4 053.000	40.5	40
206.65	5 066.250	50.7	50
209.40 (C.T.)	5 491.815	54.9	54.2 (C.P.) (3)

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/kg
115.77	109.4
117.0	108.5
119.80	107.5

Thermodynamic Properties of Krypton as Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	20.786 J/(mol·°K)
Entropy, S°	163.979 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_0^\circ)/298$	−143.193 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	6.197 6 kJ/mol

Compressibility Factors, Z = PV/RT (6)

Compressibility factors for gaseous krypton at 21.0 °C at various pressures are shown below:

Pressure kPa	bar	atm	Z
101.3	1.013	1	0.999
1 010	10.1	10	0.980
5 070	50.7	50	0.905
10 130	101.3	100	0.820
12 670	126.7	125	0.780

Matheson

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of krypton, see W. Baker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 55–57, Matheson, Lyndhurst, New Jersey.

[3] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds, 1968*, Volume 1, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[4] *Chemical Engineers' Handbook*, 4th edition, R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, editors, *1963*, p. 3–43, McGraw-Hill Book Co., Inc., New York, New York.

[5] *Argon, Helium, and the Rare Gases*, G. A. Cook, editor, *1961*, Volume 1, p. 293, Interscience Publishers, Inc., New York, New York.

[6] **Ibid.**, p. 251.

METHANE

(Synonyms: Marsh Gas; Methyl Hydride)
(Formula: CH_4)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.016 043 kg
One Mole of CH_4	0.016 043 kg
Specific Volume @ 21.1 °C, 101.325 kPa	1 479.5 dm^3/kg; 23.7 ft^3/lb
Boiling Point @ 101.325 kPa	111.66 °K; −161.5 °C; −258.7 °F
Triple Point	
Temperature	90.66 °K; −182.5 °C; −296.5 °F
Pressure	11.69 kPa; 116.9 mbar; 87.7 mmHg
Absolute Density, Gas @ 101.325 kPa @ 0 °C	0.717 4 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 0 °C (Air = 1)	0.555
Density, Liquid @ Saturation Pressure @ −161.5 °C	0.424 1 kg/l
Critical Temperature	191.05 °K; −82.1 °C; −115.8 °F
Critical Pressure	4 640 kPa; 46.4 bar; 673.1 psia; 45.8 atm
Critical Volume	6.153 dm^3/kg
Critical Density	0.162 5 kg/dm^3
Critical Compressibility Factor	0.288
Latent Heat of Fusion @ −182.5 °C	58.42 kJ/kg; 224.0 cal/mol
Flammability Limits In Air	5.0–15.4% (by volume)
Dipole Moment, Gas	0 C·m
Molar Specific Heat, Gas @ 101.325 kPa @ 26.8 °C	
@ Constant Pressure	35.941 J/(mol·°K)
@ Constant Volume	27.531 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 26.8 °C, Cp/Cv	1.305
Molar Specific Heat, Liquid @ −175.6 °C	53.72 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 26.8 °C	0.011 18 mPa·s; 0.011 18 cP
Viscosity, Liquid @ −180 °C	0.202 mPa·s; 0.202 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 26.7 °C	0.034 238 W/(m·°K); 81.83×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −180 °C	0.226 W/(m·°K); 540.2 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −180 °C	17.8 mN/m; 17.8 dyn/cm
Solubility In Water @ 101.325 kPa (partial pressure of CH_4) @ 20 °C	0.033 08 cm^3/1 cm^3
Dielectric Constant, Gas @ 101.325 kPa @ 0 °C	1.000 944
Dielectric Constant, Liquid @ −173 °C	1.70
Autoignition Temperature	810 °K; 537 °C; 999 °F
Heat of Combustion, Gas @ 25 °C and Constant Pressure	
Gross to form H_2O (liq) + CO_2 (gas)	890.36 kJ/mol
Net, to form H_2O (gas) + CO_2 (gas)	802.32 kJ/mol

Description

Methane is a colorless, flammable, nontoxic gas with a sweet, oil-type odor. Methane is the first member of the paraffin series of hydrocarbons. It is the major constituent of natural gas. The gas is normally shipped as a nonliquefied gas in high pressure cylinders at 15,620 kPa (2 265 psig) at 21.1 °C. It is occasionally shipped in bulk as a cryogenic liquid.

Specifications

Matheson supplies six grades of methane.

1. Research Grade

This grade of methane is of the highest purity that is available. Research Grade methane has a minimum purity of 99.99 mole %.

2. Matheson Purity Grade

This grade has a minimum purity of 99.99 mole %.

3. Ultra High Purity Grade

This grade of methane has a minimum purity of 99.97 mole %.

4. C. P. Grade

This grade of methane has a minimum purity of 99 mole %.

C.P. Grade methane is supplied in cylinders at 15,620 kPa (2 265 psig) and at 24,130 kPa (3 500 psig).

5. Technical Grade

This grade has a minimum purity of 98.0 mole %.

6. Commercial Grade

This grade of methane is actually Tennessee natural gas as it is received from the pipe line. There is no guaranteed purity, but the methane content usually runs 93% or better.

Tertiary-butyl mercaptan is added as an odorizer (0.6 lb/million ft^3). The sulfur content is 0.002 grains/100 ft^3. A typical gross heating value is 1044 Btu/ft^3.

Uses

Methane is useful in the testing of gas appliances which are to be used in natural gas areas. It is one of the raw materials used in the production of ethanol, methyl chloride, methylene chloride, and is also used to produce ammonia and acetylene. High purity methane is burned to form a high quality carbon black which is used in a variety of electronic components.

Effects in Man and Toxicity (2)

Methane is classified as a simple asphyxiant by the 1979 ACGIH. Methane is practically physiologically inert except when it lowers the partial pressure of oxygen in the air enough to cause systemic effects due to oxygen deficiency, e.g., nausea and pressure on the forehead and eyes. Methane has a sweet oil type of odor, but this odor provides no warning of dangerous concentrations.

First Aid Treatment (2)

The conscious person who becomes aware of any of the above symptoms should go promptly to an uncontaminated area and inhale fresh air or oxygen. However, in the event of a massive exposure the victim may become unconscious or symptoms of asphyxiation may persist. In that case the person should be removed to an uncontaminated atmosphere and given artificial respiration and then oxygen, after breathing has been restored. Treat symptomatically thereafter.

Precautions in Handling and Storage

The hazards due to the handling of methane stem mainly from its extreme flammability. Cylinders of methane should be stored in a well-ventilated area away from heat and all ignition sources such as flames and sparks. Never use flames to detect flammable gas leaks, use soap water solution. Do not use methane around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of methane cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all lines and equipment used with methane.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

All fittings and joints should be painted with soap solution to detect leaks which will be indicated by bubble formation. Never use a flame to detect leaks.

Disposal of Leaking Cylinders

Leaking cylinders may be disposed of by the procedure described in Appendix II-A.

Materials of Construction

Since methane is a noncorrosive gas, any common or commercially available metal may be used. However, piping systems or vessels to contain methane should be designed to have a working pressure as specified by competent engineers using a safety factor conforming to the ASME code for pressure piping.

Cylinder and Valve Description

DOT approved, high pressure steel cylinders are used in methane service. These cylinders usually have a service pressure of 15 620 kPa (2 265 psig). Cylinders of methane are equipped with valves with the Standard Compressed Gas Association (CGA) valve outlet No. 350 having a specification thread size of 0.825 inch diameter-14 threads per inch, left-hand external accepting a round nipple. See Figure 1 for an illustration of this valve outlet and its mating connection. This valve outlet is standard for all high pressure flammable gases. Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet and a 9/16 inch-18 threads per inch male dual valve outlet.

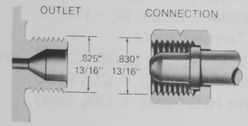


Fig. 1. CONNECTION 350 .825″-14 LH EXT. accepting Round Shaped Nipple

Safety Devices

DOT regulations require safety devices on cylinders of methane which are approved by the Bureau of Explosives. A number of approved types of safety devices may be used with methane. Two of each type are required when cylinders are over 55 inches long (exclusive of the neck). They are as follows: 73.9 °C (165 °F) fusible metal, a 100 °C (212 °F) fusible metal, a frangible disc backed up by a 73.9 °C (165 °F) fusible metal, or frangible disc with 100 °C (212 °F) fusible metal backing. Matheson employs the frangible disc with 100 °C (212 °F) fusible metal backing. This safety device is incorporated on the valves of all cylinders except lecture bottles. With this type of safety relief device it is necessary to melt the fusible metal before the frangible disc can break, allowing the gas to escape.

Recommended Controls

Automatic Pressure Regulators

In order to reduce the high cylinder pressure of methane to a safe working value consistent with a system's design, the following types of controls are recommended.

1. Single Stage Automatic Regulators

Single stage regulators will reduce cylinder pressure in one stage to a delivery pressure, in a particular range, depending upon the design of the regulator and its spring load. A single stage regulator will show a slight variation in delivery pressure as cylinder pressure falls. The following single stage regulators are available from Matheson for use with C.P. Grade, Technical Grade, and Commercial Grade methane:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
1L-350	28–550	0.28–5.5	4–80
1H-350	69–1 240	0.69–12.4	10–180
2-350	345–4 480	3.45–44.8	50–650
3-350	690–10 340	6.9–103.4	100–1 500
4-350	690–17 240	6.9–172.4	100–2 500
3320 (for lecture bottles only)	28–410	0.28–41	4–60

Single stage regulators Model 19-350 and Model 3500-350 are recommended for use with the high purity grades of methane. The Model 19 regulator is all brass construction with a diaphragm of German silver alloy (65% copper, 17% zinc, 18% nickel) with nylon seat and aluminum and nylon gaskets. It is an ideal instrument for normal laboratory use of high purity grades of methane. It is provided with packless control valve FF 939B with ¼ inch Gyrolok tube fitting. It has two 2½ inch gauges, a delivery pressure gauge of 0–690 kPa (0–100 psig or 0–1 380 kPa (0–200 psig) and a cylinder pressure range of 0–20 680 kPa (0–3 000 psig). It has a delivery pressure range of 28–345 kPa (4–50 psig) or 69–10 340 kPa (10–150 psig). The regulator can be supplied with a helium leak rate check if desired. The maximum acceptable leak rate is 2×10^{-9} cm^3 per second inboard.

The Model 3500 regulator is constructed of type 316 stainless steel. It has a type 316 stainless steel diaphragm, Tefzel seat, and Teflon gaskets. It is provided with a Model 4374 packless outlet valve with ¼ inch Gyrolok tube fitting, and stainless steel delivery pressure and cylinder pressure gauges. There are no rubber parts. It has a delivery pressure range of 28–520 kPa (4–75 psig).

2. Two Stage Regulators

This type of regulator performs the same function as a single stage regulator. However, greater accuracy and control of the delivery pressure is maintained, and the delivery pressure does not vary as cylinder pressure falls. The following two stage regulators are available from Matheson for use with C.P. Grade, Technical Grade and Commercial Grade of methane:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
8L-350	14–104	0.14–1.04	2–15
8-350	28–340	0.28–3.4	4–50
8H-350	69–690	0.69–6.9	10–100
9-350	138–1720	1.38–17.2	20–250

Two stage regulators Model 3800-350 and Model 3104-350 having delivery pressure ranges of 28–620 kPa (4–90 psig) and 28–690 kPa (4–100 psig), respectively, are recommended for use with the high purity grades of methane.

3. Controls for Methane at Special High Pressure

C.P. Grade methane is available at 24 130 kPa (3 500 psig), in addition to its normal availability at 15 620 kPa (2 265 psig). The following single stage regulators are recommended for use with 24 130 kPa (3 500 psig) cylinders.

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
3-350	690–10 340	6.9–103.4	100–1 500
4-350	690–17 240	6.9–172.4	100–2 500
3064-350	172.5–27 600	1.72–276.0	25–4 000
3075-350	1 380–41 370	13.8–413.7	200–6 000

4. Low Pressure Regulator

The above regulators are not satisfactory for accurate delivery pressures below 34.5 kPa (5 psig). Therefore, an auxiliary regulator specifically designed for low pressures is recommended for use in series with any of the standard type regulators having delivery pressures up to 1 720 kPa (250 psig).

Matheson has various models known as the Model 70 regulator which may be obtained with delivery pressures ranging from 2 inches water column to 69 kPa (10 psig) as follows:

Model No.	Delivery Pressure Range		
	kPa	mbar (g)	psig
70B	0.5–3.0	5–30	2 inches water column
70	3.4–34.5	34–345	0.5–5.0 psig
70A	34.5–68.9	345–689	5–10 psig

When this regulator is supplied for use in conjunction with a standard regulator, an extra heavy hose is available for connection between the two regulators. All Matheson regulators are provided with needle valves attached to the outside so that accurate flow control can be maintained.

Manual Controls

Manual needle valves for direct attachment to cylinder valve outlet are available. These types of controls are mainly used

for control of intermittent flows or where it is desired to control the flow of gas directly from the cylinder. This type of needle valve will allow control of extremely slow-flow rates on up to relatively large-flow rates. However, pressure cannot be controlled with such a valve, and if a line or system becomes plugged, dangerous pressures can build up. The following manual type valves are recommended for use with C.P., Technical and Commercial Grades of methane: Model 50-350 and Model 52-350 with tank gauge to indicate tank pressure. A Model 30AR or Model 31B needle valve is recommended for use with lecture bottles.

Manual control Model 4351-350 is available for use with Research Purity, Matheson Purity, and Ultra High Purity Grades of methane.

Flowmeters

Matheson Series 7600 laboratory brass or stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass or stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use with all grades of methane.

Electronic mass flowmeters, such as Matheson series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Methane is shipped in high pressure steel cylinders as a flammable compressed gas requiring a DOT "Red Gas Label". The cylinders are usually filled to the marked service pressure of the cylinder Pressurization over the marked service pressure of the cylinder is not permitted.

Commercial Preparations

Methane is obtained in pure form from natural gas wells in California. It is also purified from other natural gas wells and is also obtained from the cracking of petroleum fractions.

Chemical Properties

Methane is the first and most inert member of the saturated or paraffin (alkane) series of hydrocarbons.

Although methane is generally inert at room temperature and atmospheric pressure, it does undergo reaction under certain conditions. For example: By cracking methane-hydrogen (ratio 1:2), in an electric arc, as much as 51% of the methane is

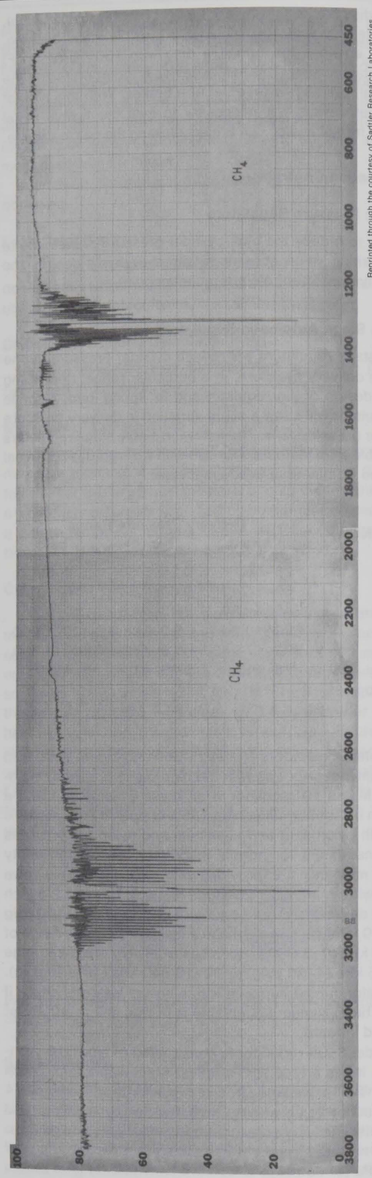


Fig. 2. High resolution infrared spectrum of gaseous methane in the frequency range 3 800-450 cm^{-1}; 10 cm path length, KBr windows; pressure: 9.33 kPa (70 mmHg) (5).

Matheson

converted to acetylene; the oxidation of methane under pressure has been investigated extensively, e.g., at 360 °C and 100 atmospheres, and a 9:1 methane-oxygen ratio, 17% of the methane was recovered as methyl alcohol, and 0.6% as formaldehyde, the remainder being carbon dioxide, carbon monoxide, and water; methane and sulfur at 700–800 °C react to form about 65% hydrogen sulfide and 30% carbon disulfide; chlorine in diffused daylight reacts with methane giving all four possible substitution products (sunlight explodes a mixture of 2 volumes of chlorine with 1 of methane); methane may be chlorinated thermally (in the absence of light and at elevated temperatures) to give 75–80% methyl chloride, or to give 90% carbon tetrachloride; methane can be nitrated but with more difficulty than ethane and propane.

Thermodynamic and Detailed Physical Data

Molecular Structure

The four valences of the carbon atom of methane are oriented according to van't Hoff's tetrahedral model, i.e., the four attached hydrogen atoms lie at the corners of a regular tetrahedron. The H—C—H bond angle in methane is 109.47°; the C—H bond distance is 1.091 A° (1.091 × 10^{-10} m). Methane is assigned to point group T_d.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous methane.

Vapor Pressure

Some vapor pressure data up to 101.325 kPa (1 atm) are shown below (3).

Temperature, °K	Vapor Pressure kPa	bar	atm
90.66	11.7	0.117	0.115
100	34.9	0.349	0.344
102.5	45.0	0.450	0.444
105	57.2	0.572	0.565
107.5	71.8	0.718	0.709
110	89.3	0.893	0.881
111.66	101.325	1.013 25	1.000

Vapor pressure data between 91.70 °K and 120.65 °K are represented by the following Antoine equation (3):

$$\log_{10} p = 6.611\ 84 - \frac{389.93}{266.0 + t}$$

in which p = mmHg and t = °C.

For vapor pressure data above 101.325 kPa (1 atm), see Table 1 and Figure 3.

Latent Heat of Vaporization @ 111.66 °K	8.180 kJ/mol (1.955 (kcal/mol) (219.4 (Btu/lb)

For latent heats of vaporization at other temperatures, see Table 1.

Thermodynamic Data

For the thermodynamic properties of saturated methane liquid and vapor and those of real gas methane, see Tables 1 and 2, respectively. For compressibility data, see Table 3.

Thermodynamic Properties of Methane As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	35.639 J/(mol·°K)
Entropy, S°	186.146 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−186.146 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	10.025 kJ/mol
Enthalpy of Formation, ΔH_f°	−74.873 kJ/mol
Free Energy of Formation, ΔF_f°	−50.815 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of methane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, 1975, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, 1977, pp. 11–16, Matheson, Lyndhurst, New Jersey.

[3] H. E. Tester in *Thermodynamic Functions of Gases*, F. Din, editor, 1961, Volume 3, p. 12, Butterworth Inc., Washington, D. C.

[4] *JANAF Thermochemical Tables*, 2nd edition, 1971, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[5] *The Sadtler Standard Spectra*, 1972, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[6] See reference 3, p. 47.

[7] See reference 3, pp. 57–59, 49–51, 60–63.

[8] See reference 3, pp. 24–25.

Matheson

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED LIQUID AND VAPOR (6)

Temperature		Pressure		Entropy kJ/(kg·°K)		Enthalpy kJ/kg		Latent Heat of Vaporization kJ/kg	Specific Volume dm^3/kg		Density kg/dm^3	
°K	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
100	−279.7	34.856	0.344	73.258	158.318	3 963.1	12 469.2	8 506.1	2.270	1 460.5	0.441	0.000 685
105	−270.7	57.249	0.565	75.914	155.775	4 235.9	12 621.0	8 385.1	2.307	1 211.6	0.433	0.000 825
110	−261.7	89.267	0.881	78.463	153.406	4 511.2	12 754.9	8 243.7	2.346	620.7	0.426	0.001 611
115	−252.7	133.648	1.319	80.919	151.231	4 789.0	12 878.4	8 089.4	2.386	428.4	0.419	0.002 334
120	−243.7	193.024	1.905	83.291	149.264	5 070.2	12 994.7	7 924.5	2.428	305.4	0.412	0.003 274
125	−234.7	270.436	2.669	85.592	147.536	5 355.5	13 104.3	7 748.8	2.473	223.9	0.404	0.004 466
130	−225.7	368.924	3.641	87.835	146.009	5 645.5	13 208.1	7 562.6	2.521	167.3	0.397	0.005 977
135	−216.7	491.933	4.855	90.031	144.566	5 940.9	13 303.4	7 362.5	2.572	127.5	0.389	0.007 843
140	−207.7	642.299	6.339	92.182	143.181	6 242.9	13 382.9	7.140.0	2.629	98.2	0.380	0.010 183
145	−198.7	823.975	8.132	94.299	141.833	6 552.1	13 444.4	6 892.3	2.693	77.5	0.371	0.012 903
150	−189.7	1 040.61	10.27	96.391	140.515	6 870.1	13 656.6	6 786.5	2.768	61.18	0.361	0.016 345
155	−180.7	1 295.95	12.79	98.466	139.218	7 198.2	13 891.3	6 693.1	2.852	48.91	0.351	0.020 446
160	−171.7	1 594.86	15.74	100.542	137.926	7 538.7	13 520.2	5 981.5	2.949	39.31	0.339	0.025 439
165	−162.7	1 939.36	19.14	102.629	136.595	7 896.5	13 500.9	5 604.4	3.059	31.81	0.327	0.031 437
170	−153.7	2 330.48	23.00	104.767	135.181	8 277.2	13 447.4	5 170.2	3.188	25.67	0.314	0.038 96
175	−144.7	2 785.42	27.49	107.018	133.637	8 688.9	13 347.0	4 568.1	3.346	20.89	0.299	0.047 87
180	−135.7	3 294.08	32.51	109.437	131.909	9 147.5	13 192.6	4 045.1	3.556	16.56	0.281	0.060 39
185	−126.7	3 865.55	38.15	112.148	129.926	9 675.5	12 964.5	3 289.0	3.887	13.08	0.257	0.076 45
191.05 (C.P.)	−115.8	4 640.69	45.80	121.754		11 652.4		0.0	6.153 5		0.162 5	

Table 2. THERMODYNAMIC PROPERTIES OF REAL GAS METHANE (7)

H, ENTHALPY, kJ/mol; S, ENTROPY, J/(mol·°K); V, SPECIFIC VOLUME, cm^3/mol

Pressure kPa	atm		Temperature, °K																												
			140	160	180	200	220	240	260	280	300	320	340	360	380	400	420	440	460	470
101.325	1	H	13.749	14.426	15.104	15.782	16.464	17.146	17.836	18.535	19.246	19.970	20.711	21.476	22.259	23.062	23.886	24.736	25.610	26.054
		S	160.247	164.808	168.783	172.339	175.561	178.531	181.293	183.887	186.355	188.740	191.000	193.175	195.267	197.317	199.326	201.292	203.217	204.179
		V	11 267	12 960	14 639	16 307	17 968	19 623	21 276	22 926	24 574	26 222	27 870	29 516	31 162	32 808	34 453	36 097	37 740	38 562
202.650	2	H	13.694	14.389	15.071	15.757	16.439	17.125	17.815	18.514	19.230	19.958	20.702	21.468	22.251	23.054	23.882	24.732	25.606	26.050
		S	154.264	158.866	162.883	166.481	169.745	172.716	175.477	178.071	180.540	182.924	185.184	187.401	189.493	191.544	193.562	195.518	197.443	198.405
		V	5 535	6 405	7 260	8 103	8 938	9 771	10 603	11 434	12 265	13 096	13 923	14 747	15 571	16 395	17 219	18 043	18 868	19 280
303.975	3	H	13.640	14.347	15.037	15.728	16.414	17.104	17.795	18.497	19.213	19.945	20.690	21.456	22.242	23.045	23.874	24.723	25.598	26.045
		S	150.750	155.394	159.494	163.134	166.440	169.452	172.255	174.891	177.360	179.745	182.004	184.222	186.314	188.364	190.414	192.380	194.305	195.267
		V	3 617	4 214	4 795	5 367	5 932	6 393	7 052	7 608	8 163	8 716	9 268	9 820	10 372	10 923	11 475	12 026	12 578	12 853
506.625	5	H	13.519	14.263	14.970	15.669	16.634	17.062	17.757	18.464	19.184	19.920	20.669	21.439	22.221	23.029	23.857	24.711	25.585	26.033
		S	146.002	150.708	154.850	158.532	161.879	164.891	167.695	170.331	172.799	175.184	177.443	179.703	181.795	183.845	185.895	187.862	189.876	190.790
		V	2 076	2 456	2 823	3 178	3 525	3 866	4 204	4 542	4 880	5 216	5 550	5 884	6 217	6 549	6 881	7 213	7 543	7 708
709.275	7	H		14.175	14.903	15.611	16.313	17.021	17.719	18.431	19.150	19.891	20.644	21.418	22.200	23.012	23.845	24.698	25.573	26.020
		S		147.319	151.712	155.519	158.908	161.921	164.766	167.402	169.912	172.297	174.598	176.816	178.950	181.000	183.050	185.016	186.983	187.987
		V		1 702	1 976	2 237	2 490	2 741	2 988	3 231	3 474	3 715	3 955	4 195	4 434	4 673	4 911	5 149	5 286	5 504
1 013.250	10	H		14.029	14.807	15.527	16.242	16.954	17.665	18.380	19.104	19.853	20.610	21.384	22.175	22.987	23.820	24.677	25.556	26.004
		S		143.511	148.323	152.298	155.728	158.825	161.670	164.306	166.858	169.243	171.544	173.803	175.937	177.987	180.079	182.046	184.012	185.016
		V		1 128	1 335	1 531	1 719	1 900	2 075	2 247	2 419	2 590	2 760	2 930	3 099	3 267	3 435	3 603	3 769	3 852
2 026.500	20	H			14.330	15.180	15.966	16.728	17.468	18.209	18.949	19.715	20.484	21.271	22.079	22.899	23.740	24.606	25.493	25.945
		S			140.373	145.227	149.118	152.423	155.394	158.197	160.833	163.302	165.645	167.862	170.038	172.130	174.222	176.230	178.197	179.201
		V			584.5	703.7	812.0	913.2	1 009	1 100	1 189	1 278	1 366	1 453	1 540	1 626	1 712	1 797	1 881	1 923
3 039.750	30	H			13 657	14.740	15.661	16.493	17.263	18.025	18.790	19.577	20.363	21 163	21.979	22.811	23.661	24.531	25.426	25.882
		S			134 055	140.582	144.892	148.532	151 628	154 431	157.067	159.620	162.004	164.264	166.440	168.573	170.707	172.757	174.766	175.770
		V			320.3	427.0	509.2	582.4	650.0	715.0	778.5	840.8	901.8	961.6	1 021	1 080	1 138	1 196	1 253	1 282
4 053.000	40	H				14.200	15.293	16.209	17.037	17.836	18.631	19.435	20.238	21.054	21.882	22.723	23.581	24.460	25.359	25.824
		S				135.269	141.043	145.227	148.490	151.377	154.139	156.733	159.159	161.502	163.720	165.937	168.113	170.205	172.255	173.259
		V				279.3	355.8	417.0	472.5	524.7	574.8	623.0	669.8	716.0	761.7	806.8	851.4	895.5	939.1	960.7
5 066.250	50	H					14.853	15.870	16.786	17.644	18.468	19.292	20.117	20.945	21.786	22.635	23.497	24.384	25.301	25.765
		S				131.419	137.695	142.214	145.896	148.992	151.796	154.431	156.900	159.285	161.586	163.887	166.063	168.197	170.289	171.293
		V				261.5	317.5	365.7	409.9	452.0	492.1	530.9	569.0	606.5	643.4	697.6	715.3	750.8	768.4	
10 132.500	100	H					12.920	14.280	15.502	16.610	17.636	18.594	19.506	20.397	21.292	22.196	23.108	24.041	24.987	25.464
		S				118.491	125.353	131.294	136.273	140.457	143.888	146.942	149.745	152.381	154.850	157.193	159.452	161.628	163.804	164.850
		V					87.82	123.9	156.1	184.6	210.4	233.8	256.0	277.4	298.1	318.2	337.7	357.0	375.9	385.2
20 265.000	200	H					11.569	12.786	13.995	15.188	16.351	17.464	18.514	19.527	20.518	21.502	22.481	23.472	24.481	24.995
		S					116.441	121.713	126.524	130.917	134.892	138.449	141.628	144.515	147.235	149.787	152.172	154.431	156.691	157.779
		V					57.61	66.35	77.12	89.65	102.3	114.8	126.9	138.6	149.9	160.8	171.5	181.9	192.2	197.4
30 397.500	300	H					11.743	12.539	13.623	14.736	15.841	16.916	17.979	19.020	20.037	21.046	22.066	23.100	24.137	24.665
		S					113.596	118.156	122.298	126.357	130.164	133.721	136.900	139.871	142.633	145.268	147.779	150.247	152.716	153.988
		V					51.63	56.32	61.99	68.55	75.61	82.98	90.45	97.92	105.3	112.7	119.9	127.0	133.9	137.3
40 530.000	400	H					11.527	12.519	13.527	14.556	15.606	16.665	17.723	18.765	19.790	20.807	21.849	22.903	23.966	24.502
		S					111.629	115.897	119.788	123.512	127.110	130.541	133.721	136.691	139.495	142.214	144.808	147.319	149.787	151.001
		V					48.40	51.87	55.74	60.05	64.73	69.68	74.77	79.94	85.15	90.40	95.67	100.9	106.1	108.7

Table 3. COMPRESSIBILITY FACTORS, Z = PV/RT, FOR METHANE (8)

Pressure			Temperature, °K				
kPa	bar	atm	273.15	298.15	323.15	373.15	423.15
101.325	1.013 25	1	0.997 6	0.998 2	0.998 8	0.999 4	0.999 8
1 010	10.1	10	0.975 9	0.981 4	0.986 9	0.993 0	0.997 0
2 030	20.3	20	0.952 1	0.963 3	0.974 3	0.986 6	0.994 0
4.050	40.5	40	0.904 4	0.927 7	0.950 6	0.974 6	0.988 9
6 080	60.8	60	0.858 7	0.895 0	0.929 0	0.964 4	0.985 4
8 110	81.1	80	0.814 7	0.862 7	0.910 4	0.956 6	0.982 7
10 133	101.3	100	0.782 6	0.849 3	0.895 6	0.950 3	0.981 5
20 260	202.6	200	0.760 5	0.820 2	0.879 3	0.953 3	0.997 2
30 400	304.0	300	0.886 6	0.918 8	0.950 6	1.006 7	1.045 4
40 530	405.3	400	1.045 4	1.054 7	1.063 5	1.088 8	1.111 5
60 800	608.0	600	1.367 4	1.349 1	1.320 1	1.295 3	1.283 8
81 060	810.6	800	1.685 2	1.644 7	1.583 6	1.515 7	1.470 4
101 325	1 013.2	1 000	1.995 1	1.934 0	1.840 9	1.734 7	1.661 5

Matheson

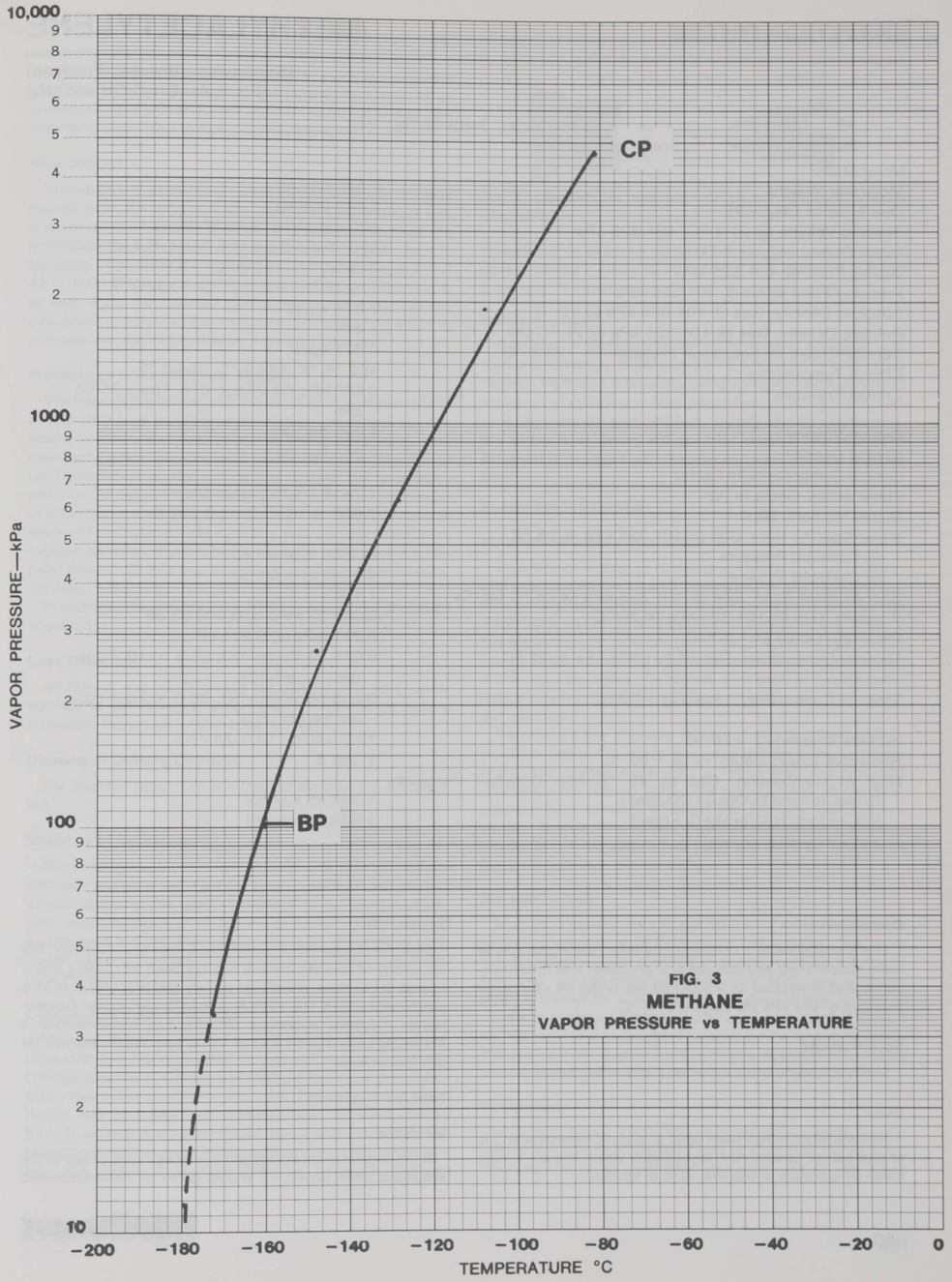


FIG. 3
METHANE
VAPOR PRESSURE vs TEMPERATURE

METHYLACETYLENE

(Synonyms: Allylene; Propyne)
(Formula: $CH_3C{:}CH$ or C_3H_4)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.040 065 kg
One Mole of $CH_3C{:}CH$	0.040 065 kg
Specific Volume @ 21.1 °C, 101.325 kPa	602.4 dm^3/kg; 9.65 ft^3/lb
Vapor Pressure @ 21.1 °C	520 kPa; 5.2 bar; 74.7 psia; 5.1 atm
Boiling Point @ 101.325 kPa	249.93 °K; −23.2 °C; −9.8 °F
Freezing Point In Air @ 101.325 kPa	170.45 °K; −102.7 °C; −152.9 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	1.671 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.411
Density, Liquid @ Saturation Pressure @ −23.2 °C	0.671 kg/l
Critical Temperature	402.38 °K; 129.2 °C; 264.6 °F
Critical Pressure	5 628 kPa; 56.28 bar; 816.2 psia; 55.54 atm
Critical Volume	4.093 dm^3/kg
Critical Density	0.245 kg/dm^3
Critical Compressibility Factor	0.276
Flammability Limits In Air	1.7–11.7% (by volume)
Dipole Moment, Gas	2.605×10^{-30} C·m; 0.781 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	61.505 J/(mol·°K)
@ Constant Volume	53.190 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C Cp/Cv	1.156
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.008 33 mPa·s; 0.008 33 cP
Viscosity, Liquid @ −20 °C	0.211 mPa·s; 0.211 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.016 23 W/(m·°K); 38.8×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −20 °C	0.015 06 W/(m·°K); 36.0×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −20 °C	18.0 mN/m; 18.0 dyn/cm
Refractive Index, Liquid, n_D @ −40 °C	1.386 3
Heat of Combustion, Gas @ 25 °C and Constant Pressure	
Gross, to form H_2O(liq)+CO_2(gas)	1 937.65 kJ/mol
Net, to form H_2O(gas)+CO_2(gas)	1 849.62 kJ/mol

Description

Methylacetylene is a colorless, nontoxic, flammable gas at room temperature and atmospheric pressure. It is readily liquefied and is shipped as a liquefied gas under its own vapor pressure of 414 kPa (60 psig) at 21.1 °C.

Specifications

Methylacetylene has a minimum purity of 96.0 mole %.

Uses

Methylacetylene has been used in organic synthesis and is of interest for special fuel applications which require a high flame temperature or extreme ease of ignition.

Toxicity (2)

Methylacetylene is not considered a toxic gas. However, the toxicology of methylacetylene has not been thoroughly investigated. It has some anesthetic activity and probably acts as a simple asphyxiant. The 1979 American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a Threshold Limit Value (TLV) of 1 000 ppm (1650 mg/m^3) for methylacetylene.

First Aid Treatment

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration and oxygen simultaneously. Treat symptomatically thereafter.

Skin Contact

In case of skin contact with liquid methylacetylene, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The hazards associated with the handling of methylacetylene arise mainly from its extreme flammability. Store and use cylinders of methylacetylene in well-ventilated areas away from heat and ignition sources such as flames and sparks. Never use flames to detect leaks of methylacetylene, use soap water solution. Do not use methylacetylene around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of methylacetylene cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all lines and equipment used to handle methylacetylene.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

All fittings and joints should be painted with soap water solution to detect leaks, which will be indicated by bubble formation. Never use a flame to detect leaks.

Disposal of Leaking Cylinders

For disposal procedure see method described in Appendix II-A.

Materials of Construction

Since methylacetylene is noncorrosive, any common or commercially available metal except copper, silver, or magnesium or their alloys may be used as materials of construction. However, piping systems or equipment to contain the gas should be designed to have a working pressure as specified by competent engineers using a safety factor conforming to the ASME code for pressure piping.

Cylinder and Valve Description

Methylacetylene is shipped in DOT approved, low pressure, steel cylinders having a rated service pressure of 1 034 kPa (150 psig) or more. Cylinders of methylacetylene are equipped with valve outlet connection No. 510. The valve outlet has a thread size of 0.885 inch diameter, with left-hand internal threads accepting a bullet-shaped nipple (see Figure 1 for an illustration). Valves used in this service are of the diaphragm type and contain no packing. They are, therefore, relatively leak-free and require no packing adjustments. Lecture bottles have a special 5/16 inch 32 threads per inch, female outlet and a 9/16 inch 18 threads per inch male dual valve outlet.

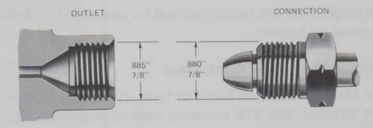


Fig. 1. CONNECTION 510 .885"-14 LH INT. accepting a Bullet Shaped Nipple

Safety Devices

Cylinders of methylacetylene were formerly equipped with fusible metal plugs, melting about 73.9 °C (165 °F), as safety devices. Matheson is presently using spring-loaded safety relief valves on all cylinders of methylacetylene. If the cylinder pressure becomes dangerously high, usually due to overheating, the safety relief device will open (at about 2 590 kPa) (375 psig) and release gas until the pressure again returns to a safe level.

Recommended Controls

Automatic Pressure Regulators

Satisfactory regulation of methylacetylene can be achieved with regulator Model 12-510. The regulator has anodized aluminum body, type 316 stainless steel internal parts, a Neoprene diaphragm, and a Teflon seat. The delivery pressure range of this regulator is 28–550 kPa (4–80 psig). Accurate flow control can be obtained with the stainless steel needle valve installed in the regulator outlet. To prevent suckback of foreign materials, a stainless steel check valve is recommended for use with the regulator.

Satisfactory low pressure regulation can be obtained with regulator Model 71, which has an aluminum body, a Teflon-faced Butyl rubber diaphragm, a Teflon seat, and type 303 stainless steel internal parts. The regulator has an oversize, pancake body to allow sensitive and accurate low pressure control. Models 71-510 and 71A-510 with delivery pressure ranges of 3.4–55 kPa (0.5–8 psig) and 34.5–83 kPa (5–12 psig), respectively, are available.

Manual Controls

Matheson needle valve Model 55-510 of monel is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, ¼" compression fitting, or ¼" NPT male or female pipe. It should be used only where manual flow control is needed and should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. A Model 60L needle valve is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory stainless steel flowmeter units with 65 mm tubes

with a single float are recommended for use where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Methylacetylene is classified by the DOT a flammable compressed gas and is shipped with the required "Red Gas Label".

Chemical Preparation

Methylacetylene can be prepared by methylation of monosodium acetylide with methyl iodide, methyl bromide, or dimethyl sulfate in liquid ammonia, toluene, or xylene or by elimination of two moles of hydrogen halide from a vicinal dihalide, such as 1,2-dibromopropane, or a geminal dihalide, such as 1,1-dibromopropane, by means of alcoholic potassium hydroxide.

Chemical Properties

Methylacetylene undergoes the typical reactions of the acetylenic hydrocarbons. Also, it undergoes isomerization at 200–400 °C in the presence of silicates to form propadiene. In the presence of boron trifluoride ether complex, it combines with anhydrous acetic acid and with methanol to form acetone dimethyl acetal. In liquid ammonia it forms a sodio derivative with sodium amide. With ethylmagnesium bromide if forms a Grignard reagent which reacts with formaldehyde and ethylene oxide to give 3-butyn-1-ol and 3-pentyn-1-ol, respectively.

Thermodynamic and Detailed Physical Data

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous methylacetylene.*

Vapor Pressure (3)

Vapor pressure of methylacetylene up to 101.325 kPa (760 mmHg) is shown below:

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
162.15	0.133	1.33	1
175.65	0.667	6.67	5
182.65	1.33	13.3	10
190.25	2.67	26.7	20
198.85	5.33	53.3	40
204.35	8.00	80.0	60
211.85	13.33	133.3	100
223.35	26.66	266.6	200
235.95	53.33	533.3	400
249.85	101.325	1 013.25	760

Vapor pressures above 101.325 kPa (1 atm) are shown below (4).

Temperature, °K	Vapor Pressure kPa	bar	atm
249.85	107.325	1.013 25	1
266.05	202.65	2.03	2
292.65	506.63	5.07	5
316.95	1 013.25	10.1	10
347.15	2 026.50	20.3	20
367.15	3 039.75	30.4	30
384.65	4 053.00	40.5	40
398.15	5 066.25	50.7	50

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv,kJ/kg
233.15	570.0
249.93	548.0
273.15	514.6

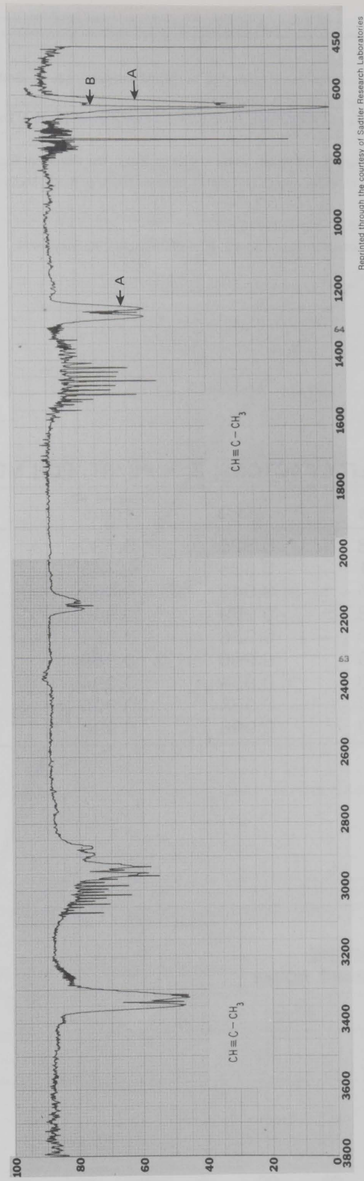
Thermodynamic Data

Compressibility data for methylacetylene are shown in Table 1.

Thermodynamic Properties of Methylacetylene As Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	60.668 J/(mol·°K)
Entropy, S°	248.111 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_{273}^\circ$	1.476 5 kJ/mol
Enthalpy of Formation, ΔH_f°	185.431 kJ/mol
Gibbs Energy of Formation, ΔG_f°	193.774 kJ/mol

* Absorbance at 730 cm^{-1} due to acetylene as impurity.



Reprinted through the courtesy of Sadtler Research Laboratories

©Sadtler 1972

Fig. 2. Infrared spectrum of gaseous methylacetylene in the frequency range of 3 800 to 450 cm^{-1}; 10 cm path length cell, with KBr optics; cell pressure: curve A (complete scan): 5.33 kPa (40 mmHg); curve B (partial scan): 0.53 kPa (4 mmHg) (6).

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of methylacetylene, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Sugel, *Effects of Exposure To Toxic Gases—First Aid and Medical Treatment, 2nd edition, 1977*, pp. 11-16, Matheson, Lyndhurst, New Jersey.

[3] *Handbook of Physics and Chemistry*, 54th edition, R. C. Weast, editor, *1973*, p. E-63, The Chemical Rubber Company, Cleveland, Ohio.

[4] *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p. 3-62, McGraw-Hill Book Company, New York, New York.

[5] K. A. Kobe and E. G. Ling, *Petroleum Refiner* 28, 133-136 (1946).

[6] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Table 1. COMPRESSIBILITY FACTORS, Z = PV/RT, FOR METHYLACETYLENE

Temperature, °K	Pressure, kPa 101.325	1 013.25	2 066.5	4 053.0	5 070.0
273.15	0.988	0.825	0.730	0.575	0.420
298.15	0.991	0.835	0.745	0.585	0.430
400	0.995	0.943	0.863	0.707	0.534
500	0.998	0.969	0.943	0.876	0.840
600	0.999	0.986	0.974	0.948	0.938
700	1.000	0.990	0.989	0.977	0.973
800	1.000	0.994	0.994	0.992	0.990
900	1.000	0.995	0.995	0.993	0.991
1 000	1.000	0.996	0.996	0.994	0.992

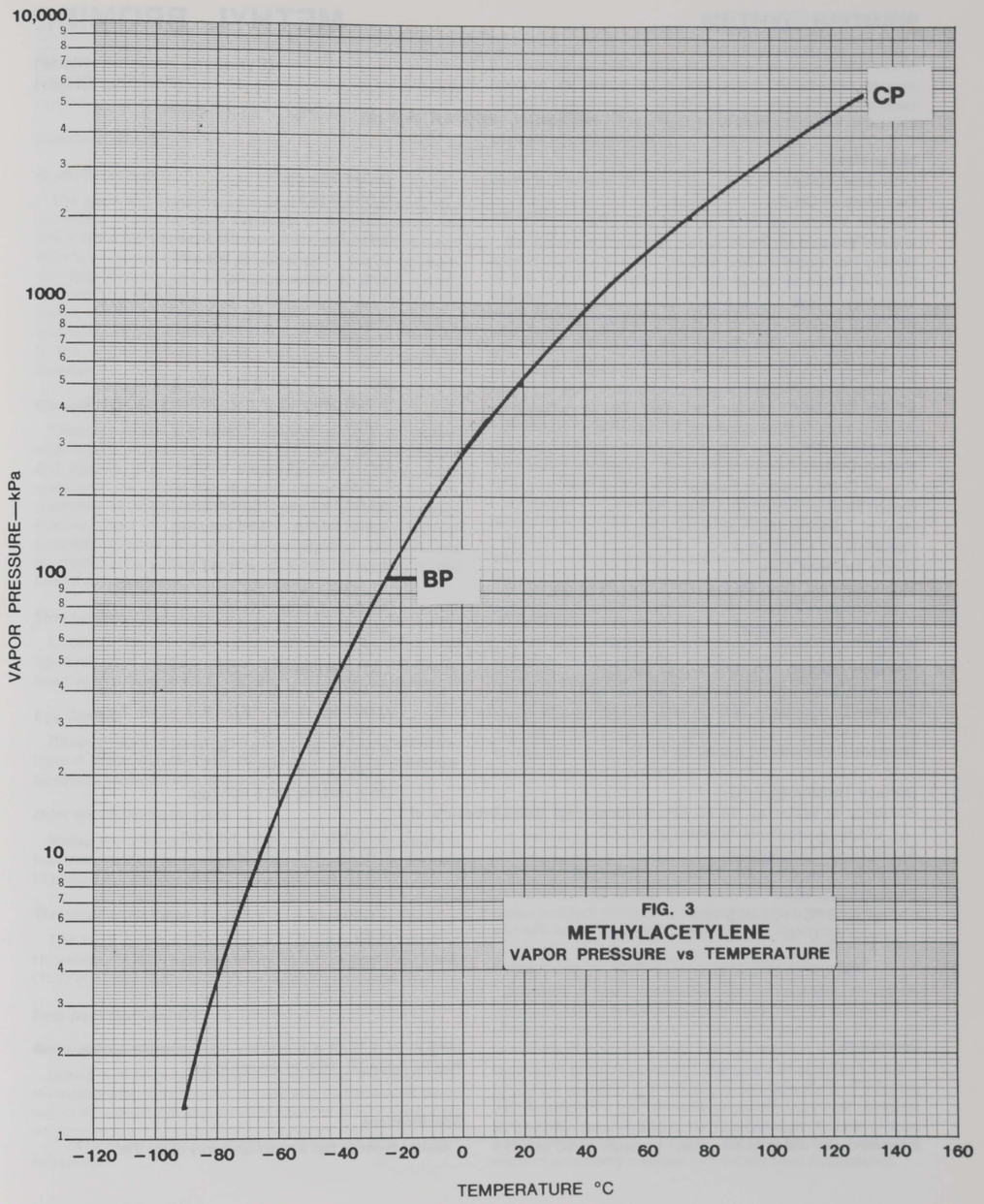


FIG. 3
METHYLACETYLENE
VAPOR PRESSURE vs TEMPERATURE

METHYL BROMIDE

(Synonym: Bromomethane)
(Formula: CH_3Br)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.094 939 kg
One Mole of CH_3Br	0.094 939 kg
Specific Volume @ 21.1 °C, 101.325 kPa	256.0 dm^3/kg; 4.1 ft^3/lb
Vapor Pressure @ 21.1 °C	191 kPa; 1.91 bar; 27.7 psia; 1.88 atm
Boiling Point @ 101.325 kPa	276.71 °K; 3.56 °C; 38.4 °F
Freezing Point In Air @ 101.325 kPa	179.55 °K; −93.6 °C; −136.5 °F
Transition Point	173.74 °K; −99.4 °C; −146.9 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	3.974 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	3.355
Density, Liquid @ Saturation Pressure @ 25 °C	1.661 7 kg/l
Critical Temperature	467.15 °K; 194.0 °C; 381.2 °F
Critical Pressure	5 220 kPa; 52.2 bar; 757.0 psia; 51.5 atm
Critical Volume	1.639 dm^3/kg
Critical Density	0.610 kg/dm^3
Critical Compressibility Factor	0.209
Latent Heat of Fusion @ −93.6 °C	62.987 kJ/kg; 15.054 kcal/kg
Heat of Transition @ −99.4 °C	4.998 kJ/kg; 1.195 kcal/kg
Flammability Limits In Air	10–16% (by volume)
Dipole Moment, Gas	6.04×10^{-36} C·m; 1.81 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	45.020 J/(mol·°K)
@ Constant Volume	36.704 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.227
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.012 50 mPa·s; 0.012 50 cP
Viscosity, Liquid @ Saturation Pressure @ 0 °C	0.380 mPa·s; 0.380 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.007 95 W/(m·°K); 19.0×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ 0 °C	0.034 0 W/(m·°K); 81.3×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 0 °C	25.5 mN/m; 25.5 dyn/cm
Solubility In Water @ 99.73 kPa (748 mmHg) (total pressure of CH_3Br + aqueous tension) @ 20 °C	1.75 kg/100 kg of solution
Autoignition Temperature	810 °K; 537 °C; 999 °F
Refractive Index, Liquid @ Saturation Pressure, n_D @ 25 °C	1.418 7
Dielectric Constant	
Gas @ 0 °C, 101.325 kPa	1.000 944
Liquid @ 0 °C	9.82

Description

Methyl bromide is a colorless, poisonous gas at room temperature and atmospheric pressure. It is odorless except in relatively high concentrations where it has a chloroform-like odor. It is easily liquefied and is shipped in steel cylinders as a liquefied gas under its own vapor pressure of 90 kPa (13 psig) at 21.1 °C. It is practically nonflammable except in the narrow range 10–16% by volume in air.

Specifications

Methyl bromide has a minimum purity of 99.5%.

Uses

Methyl bromide is used in organic synthesis; as a low-boiling solvent; as a refrigerant; and as a fumigant.

Effects In Man (2)

Acute Poisoning

The signs and symptoms of methyl bromide poisoning vary according to the degree of exposure. In most instances, the onset of the symptoms is delayed and this latent period varies from ½ to several hours and occasionally 12, 24, or 48 hours. The symptoms may be fatigue, headache, dizziness, nausea and vomiting, disturbances of hearing and vision, mental confusion, muscular weakness, collapse, respiratory difficulties and coma. Death is usually due to lung damage, but damage to the central nervous system may accompany pulmonary damage.

Chronic Poisoning

Exposure to low, but harmful, concentrations of methyl bromide over a period of time results in a varied picture of signs and symptoms. In order of frequency of occurrence, these symptoms are: visual disturbances, disturbances of speech, numbness of the extremities, mental confusion, hallucinations, tremors, coma and frequent fainting attacks. Most symptoms disappear in a few days after discontinuance of exposure, but numbness of the extremities and visual disturbance may persist from 2 to 5 months.

Skin Contact

Contact of the skin with high concentrations of vapor or with liquid methyl bromide produces a tingling and burning sensation followed by erythema, vesication and blister formation.

Eye Contact

Direct contact of liquid methyl bromide, or high concentrations of vapor, with the eyes or eyelids can produce temporary blindness, conjunctivitis, and edema of the eyelids.

Odor and Warning Property

Methyl bromide has practically no odor or irritating effects in low concentration and therefore does not provide any warning of physiologically dangerous concentrations.

Threshold Limit Value (T.L.V.)

The 1979 American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a Threshold Limit Value (TLV) of 15 ppm (60 mg/m^3)* for methyl bromide (skin).

First Aid Treatment (2)

General Procedure

Speed is of primary importance in removing the victim from a contaminated atmosphere, in removing contaminated clothing, or in removing methyl bromide from the skin or eyes. First aid must be started at once in all cases of contact with methyl bromide as serious injury may result. All affected persons should be referred to a physician even when immediate injury is not apparent. The physician should be given a detailed account of the accident.

Specific Procedures

Inhalation

Symptoms of moderate methyl bromide poisoning will disappear on discontinuation of the exposure and prompt removal of the victim to fresh air. In more severe poisoning (acute exposure to concentrations of 200 ppm or higher), the victim should be removed promptly to an uncontaminated atmosphere and given immediate attention. Symptoms of headache, nausea, vomiting, or dizziness should be taken as indication for immediate treatment. The victim should be kept at absolute rest for at least 48 hours. Oxygen (100%) inhalation should be started at once, even though there are no signs of lung injury, and should be given for 30 minutes of each hour for 6 hours. Oxygen administration should be given against a positive pressure of 3–4 cm of water, obtained by immersing the exhalation tube into water to this extent.

If respiration is weak or fails, artificial respiration should be started with simultaneous administration of oxygen.

Under no circumstances should a worker be allowed to return to work before he has been examined by a physician and found to be free of residual signs of injury.

Skin Contact

In case of contamination of shoes or other articles of clothing with liquid methyl bromide, all such clothing must be removed at once and the skin washed with copious quantities of water and then with a 2% aqueous solution of sodium bicarbonate. The contaminated clothing must not be worn again until washed thoroughly and dried. Skin lesions should be bathed in sodium bicarbonate solution and the blisters should be treated like second degree thermal burns.

Contact with Eyes

If methyl bromide in liquid form or in high concentrations comes in contact with the eyes, the eyes should be irrigated immediately with copious quantities of water for a minimum of 15 minutes. The eyelids should be held apart during the irrigation to insure contact of the water with all tissues of the eyes and lids. Medical attention should be obtained promptly.

Suggestions for Medical Treatment After Inhalation

In cases of frank pulmonary edema, venesection may be indicated. Mild convulsions may be controlled by judicious use of short-acting barbiturates. If the liver is enlarged or the victim complains of epigastric pain, glucose solution may be administered intravenously, but this should be given only if there is no danger of pulmonary edema. Do not give drugs which may interfere with the respiratory center or with proper oxygenation of the blood (e.g., morphine, barbiturates or sulfa drugs). Drugs needed for control of secondary infection are best used when signs of circulatory collapse and anoxia have disappeared.

* 1979 ACGIH Notice of Intent to Change to 5 ppm (20 mg/m^3) (skin).

Precautions in Handling and Storage

(a) Methyl bromide process vessels and cylinders should be isolated from materials of a flammable nature.

(b) Rapid-action safety-showers and eye-washing facilities should be available in readily accessible locations in the areas where methyl bromide is being handled.

(c) Employees who handle methyl bromide should be provided with the following equipment: high-top safety shoes and woolen outer clothing; suitable gas-tight chemical safety goggles when working in a hood or a full face gas mask when not working in a hood; plastic gloves or gloves made of canvas and covered with plastic (rubber and leather gloves are unsatisfactory).

(d) Industrial canister type gas masks and air or oxygen supplied masks approved by NIOSH for methyl bromide should be kept available for use in convenient locations in emergencies.

(e) All federal, state, and local regulations regarding health and pollution should be observed when venting methyl bromide from process vessels or containers.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks of methyl bromide vapor from process lines may be detected by applying soap water solution to the site of the suspected leaks; leaks will be evident by the formation of bubbles at the leak site. As a rough determination of the presence or absence of harmful concentrations of methyl bromide vapor in the atmosphere, a halide detector may be employed.

Matheson has available a Toxic Gas Detector Model 8014K for detection of methyl bromide in air. A 100 cm^3 sample of the atmosphere is drawn through a Model 157Sb (5--80 ppm) detector tube which contains a chemical reagent that absorbs and reacts with the methyl bromide. The length of the resulting color stain and, hence, the concentration is read directly off the detector tube.

Disposal of Leaking Cylinders

Since methyl bromide is freely soluble in such organic solvents as ethyl alcohol, chloroform, carbon tetrachloride, benzene, and toluene, it can be absorbed in any of these solvents and recovered from the solution for utilization.

Materials of Construction

Methyl bromide is not particularly corrosive to most metals. It is noncorrosive when dry. However, it attacks aluminum and aluminum alloys (which should not be used as materials of construction) with the formation of aluminum trimethyl, which is spontaneously flammable.

Cylinder and Valve Description

Methyl bromide is shipped in DOT approved, low pressure steel cylinders. The cylinder valve is of brass and has a Compressed Gas Association (CGA) valve outlet and connection No. 320. This valve outlet is 0.825 inch in diameter with right-hand external threads, with a flat seat and used with a washer to seal (see Figure 1 for illustration of this outlet and mating connection). The present CGA standard for methyl bromide is valve outlet connection No. 330. Lecture bottles have 5/16 inch-32 threads per inch, female outlet.

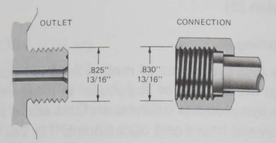


Fig. 1. CONNECTION 320 .825"-14 RH EXT. used with Flat Seat and Washer

Safety Devices

No safety devices are required or used in cylinders containing methyl bromide. Precautions are, therefore, required to keep all sources of heat away from cylinders to prevent dangerous hydrostatic pressures from building up.

Recommended Controls

Manual Controls

Matheson needle valve Model 50-320, a brass bar stock valve, is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, ¼" compression fitting, or ¼" NPT male or female pipe. It should be used only where manual flow control is needed and should not be used as a pressure control, since it will not prevent pressure from building up if a system becomes clogged, or if the system itself is closed. A Model 31B manual needle valve can be supplied for use with lecture bottles, where accurate flow control is desired.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass flowmeter units with 65 mm tubes with single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Matheson

Shipping Regulations

Methyl bromide liquid is classified by DOT as a Class B poison and is shipped with the required "Poison Label"

Commercial Preparation

Methyl bromide is obtained from methanol and hydrobromic acid in the presence of dehydrating agents or in the presence of catalysts.

Chemical Properties

Some typical reactions of methyl bromide of wide use in organic synthesis are as follows: It reacts with magnesium to form the Grignard reagent. It reacts with sodium (Wurtz synthesis), with alkali alkoxides (Williamson synthesis), with ammonia, with alkali hydrosulfides, with metal cyanides, with salts of carboxylic acids, and with sodio derivatives of active methylene compounds and acetylene compounds. Methyl bromide undergoes a variety of other nucleophilic displacement reactions.

Thermodynamic and Detailed Physical Data

Molecular Structure

Replacement of one of the hydrogens of methane by bromine results in distortion of the original tetrahedral symmetry of the methane molecule. Because of the electronegative character of the bromine atom, methyl bromide has a permanent dipole moment with the bromine atom the negative end of the dipole. Methane which is a symmetrical molecule has no permanent dipole moment. Methyl bromide belongs to point group C_{3v} and has a symmetry number of three.

Infrared Spectrum

See Figure 2 for infrared spectrum of gaseous methyl bromide.

Vapor Pressure

Vapor pressure data up to 1 500 mmHg have been calculated by the following Antoine vapor pressure equation (3).

$$\log_{10}p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10}p} - C$$

in which t = °C and p = mmHg, and the constants A, B, and C have the values of 6.959 65, 986.590, and 238.32, respectively.

Some calculated vapor pressure values are shown below:

Temperature		Vapor Pressure		
°K	°F	kPa	mbar	mmHg
200.37	−99.00	1.33	13.3	10
209.18	−83.15	2.67	26.7	20
218.98	−65.51	5.33	53.3	40
225.24	−54.24	8.00	80.0	60
233.75	−38.92	13.33	133.3	100
246.61	−15.77	26.66	266.6	200
254.93	−0.80	40.00	400.0	300
261.24	10.56	53.33	533.3	400
266.39	19.83	66.66	666.6	500

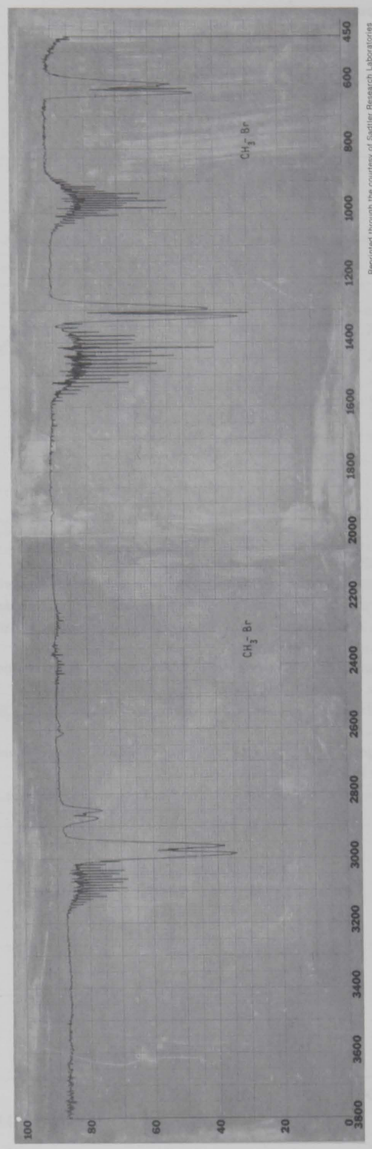


Fig. 2. Infrared spectrum of gaseous methyl bromide in the frequency range of 3 800 cm^{-1} to 450 cm^{-1}; 10 cm path length cell, with KBr optics; cell pressure: 6.666 kPa (50 mmHg) (6).

Matheson

METHYL BROMIDE

Temperature °K	Temperature °F	Vapor Pressure kPa	Vapor Pressure mbar	Vapor Pressure mmHg
270.77	27.72	79.99	799.9	600
274.61	34.63	93.33	933.3	700
276.71	38.41	101.325	1 013.25	760
278.04	40.80	106.7	1 067	800
281.14	46.38	120.0	1 200	900
283.99	51.51	133.3	1 333	1 000
289.08	60.67	160.0	1 600	1 200
295.59	72.39	200.0	2 000	1 500

Vapor pressures above 101.325 kPa (1 atm) are shown below (4).

Temperature, °K	Vapor Pressure kPa	Vapor Pressure bar	Vapor Pressure atm
276.75	101.325	1.013 25	1
296.45	203	2.03	2
327.95	507	5.07	5
357.15	1 010	10.1	10
394.85	2 030	20.3	20

Temperature, °K	Vapor Pressure kPa	Vapor Pressure bar	Vapor Pressure atm
420.65	3 040	30.4	30
443.35	4 050	40.5	40
463.15	5 070	50.7	50

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/kg
253.15	263.59
273.15	253.13
276.71	252.00

Thermodynamic Properties of Methyl Bromide As Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	42.426 J/(mol·°K)
Entropy, S°	246.270 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	10.611 kJ/mol
Enthalpy of Formation, ΔH_f°	−35.15 kJ/mol
Gibbs Energy of Formation, ΔG_f°	−25.94 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of methyl bromide, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 91-95, Matheson, Lyndhurst, New Jersey.

[3] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds, 1968*, Volume 1, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[4] *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p. 3-62, McGraw-Hill Book Co., Inc., New York, New York.

[5] D. D. Wagman, *et al.*, *Selected Values of Chemical Thermodynamic Properties, 1968*, p. 118, Natl. Bur. Stand. Tech. Note 270-3, U. S. Government Printing Office, Washington, D. C.

[6] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

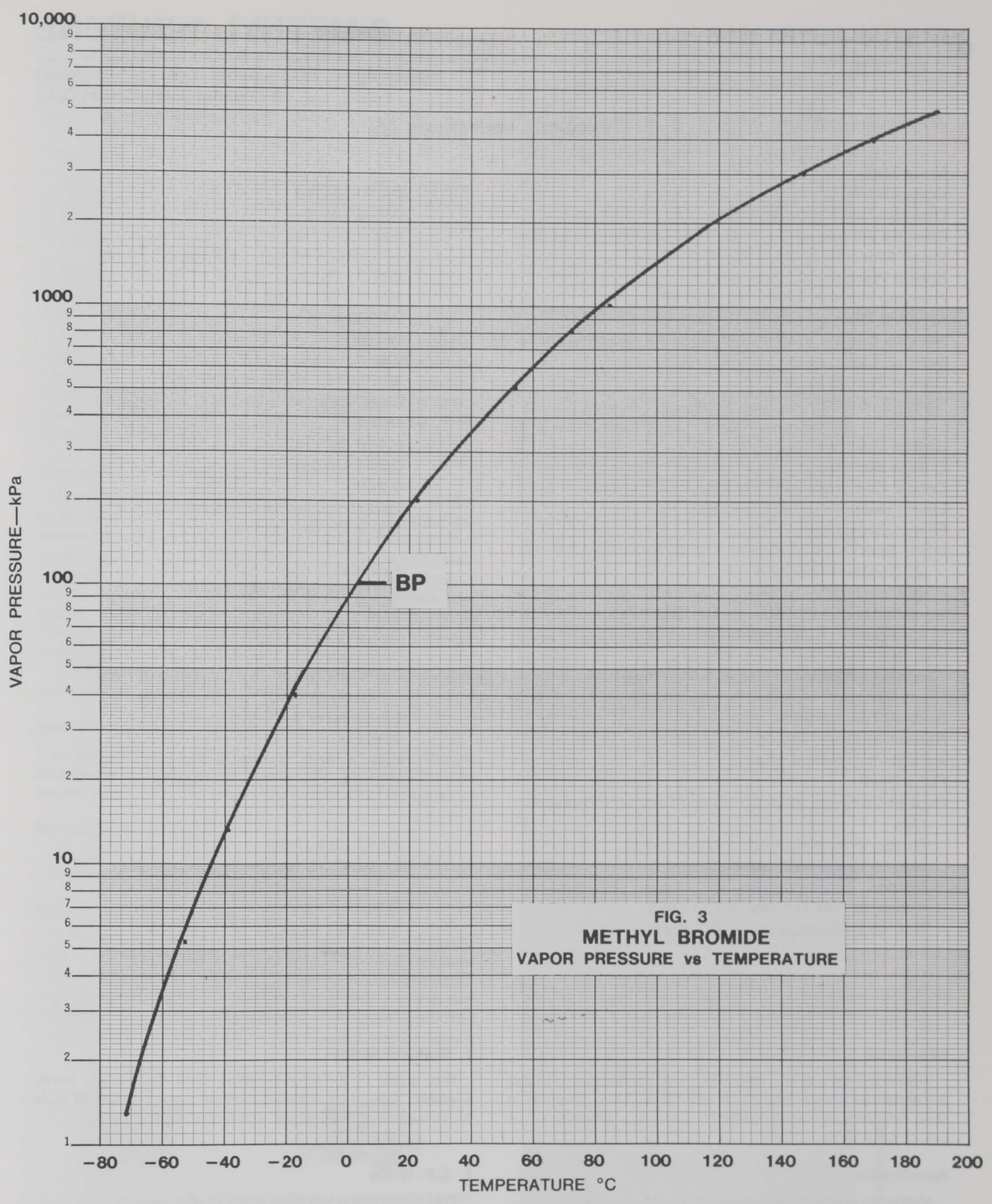


FIG. 3
METHYL BROMIDE
VAPOR PRESSURE vs TEMPERATURE

3-METHYL-1-BUTENE

(Synonyms: Isoamylene; Isopropylethylene)
(Formula: $(CH_3)_2CHCH{:}CH_2$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.070 135 kg
One Mole of $(CH_3)_2CHCH{:}CH_2$	0.070 135 kg
Specific Volume @ 21.1 °C, 101.325 kPa	343.3 dm^3/kg; 5.5 ft^3/lb
Vapor Pressure @ 21.1 °C	115 kPa; 1.15 bar; 16.7 psia; 1.14 atm
Boiling Point @ 101.325 kPa	293.21 °K; 20.1 °C; 68.1 °F
Freezing Point In Air @ 101.325 kPa	104.71 °K; −169.0 °C; −272.2 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	2.993 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	2.526
Density, Liquid @ 20 °C	0.627 2 kg/l
Critical Temperature	453.15 °K; 180.0 °C; 356.0 °F
Critical Pressure	3 630 kPa; 36.3 bar; 526.1 psia; 35.8 atm
Critical Volume	4.149 dm^3/kg
Critical Density	0.241 kg/dm^3
Critical Compressibility Factor	0.280
Latent Heat of Fusion @ −169.0 °C	76.475 kJ/kg; 18.278 kcal/kg
Flammability Limits In Air	1.5–9.1% (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ 15.6 °C	
@ Constant Pressure	115.500 J/(mol·°K)
@ Constant Volume	107.195 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 15.6 °C, Cp/Cv	1.077
Molar Specific Heat, Liquid @ 16.6 °C	153.395 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.007 53 mPa·s; 0.007 53 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.015 06 W/(m·°K); 36.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 20 °C	14.3 mN/m; 14.3 dyn/cm
Refractive Index, Liquid, n_D @ 20 °C	1.364 3
Autoignition Temperature	638 °K; 365 °C; 689 °F
Flash Point	< 266 k; < −7 °C; < −19.4 °F
Heat of Combustion @ 25 °C and Constant Pressure	
Gas	
Gross, to form H_2O(liq) + CO_2(gas)	3 367.83 kJ/mol
Net, to form H_2O(gas) + CO_2(gas)	3 147.75 kJ/mol
Liquid	
Gross, to form H_2O(liq) + CO_2(gas)	3 343.98 kJ/mol
Net, to form H_2O(gas) + CO_2(gas)	3 123.90 kJ/mol

Description

3-Methyl-1-butene is a colorless nontoxic, flammable gas at temperatures above 293.21 °K (20.06 °C). It is shipped in steel cylinders as a liquid under its own vapor pressure of 14 kPa (2 psig) at 21.1 °C.

Specifications

Matheson supplies two grades of 3-methyl-1-butene.

1. Research Grade

This grade of 3-methyl-1-butene is of the highest purity available. Typical lot analyses indicate a purity of 99.92 mole %. This material is furnished with a statement of purity.

2. C.P. Grade

This grade has a minimum purity of 99.0 mole %.

Matheson

Uses

3-Methyl-1-butene is used in organic synthesis and in the manufacture of high-octane fuel.

Toxicity

The toxicity of 3-methyl-1-butene has not been thoroughly investigated. It probably has some anesthetic activity and can act as a simple asphyxiant by displacing the necessary amount of oxygen to support life.

First Aid Treatment

Inhalation

If the subject is conscious and becomes dizzy or nauseous, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration and oxygen simultaneously. Treat symptomatically thereafter.

Precautions in Handling and Storage

The hazards in handling 3-methyl-1-butene are mainly due to its flammability. Store and use cylinders of 3-methyl-1-butene in well-ventilated areas away from heat and all sources of ignition such as flames and sparks. Never use flames to detect flammable gas leaks, use soapy water. Do not store reserve stocks of cylinders of 3-methyl-1-butene with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all lines and equipment used with 3-methyl-1-butene.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks in lines and equipment containing 3-methyl-1-butene may be detected by applying soap water solution to the suspected points: leaks will be indicated by bubble formation.

Materials of Construction

Since 3-methyl-1-butene is noncorrosive, any common or commercially available metal may be used.

Cylinder and Valve Description

3-Methyl-1-butene is packed in DOT approved, low pressure steel cylinders. Cylinders of 3-methyl-1-butene are equipped with valves having Compressed Gas Association (CGA) standard valve outlet connection No. 510, which have a thread size of 0.885 inch diameter with left-hand internal threads accepting a bullet-shaped nipple (see Figure 1). Lecture bottles have a

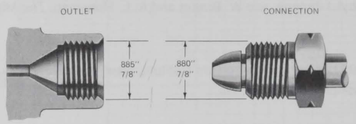
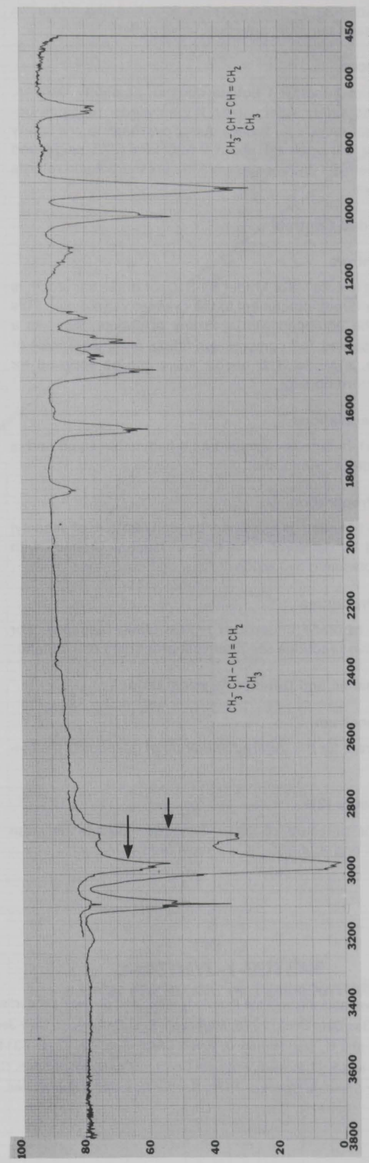


Fig. 1. CONNECTION 510 .885″-14 LH INT. accepting a Bullet Shaped Nipple



Reprinted through the courtesy of Sadtler Research Laboratories
© Sadtler 1972

Fig. 2. Infrared spectrum of gaseous 3-methyl-1-butene over the frequency range of 3 800 cm^{-1} to 450 cm^{-1}; 10 cm path length cell, with KBr optics; cell pressure: curve A (complete scan): 6.667 kPa (50 mmHg), curve B (partial scan): 0.667 kPa (5 mmHg) (4).

Matheson

special 5/16 inch-32 threads per inch, female outlet and a 9/16 inch-18 threads per inch male dual valve outlet.

Safety Devices

Cylinders of 3-methyl-1-butene contain, as safety devices, spring-loaded safety relief valves. If the cylinder pressure becomes dangerously high, usually due to overheating, the safety relief device will open (at about 2 590 kPa (375 psig)) and release 3-methyl-1-butene gas until the pressure again returns to a safe level.

Recommended Controls

Manual Controls

Matheson needle valve Model 50-510, of brass bar stock, is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a serrated hose end, ¼" compression fitting, or ¼" NPT male or female pipe. A Model 31B needle valve can be supplied for use with lecture bottles.

Shipping Regulations

3-Methyl-1-butene is classified as a flammable liquid and is shipped under a "Red Label".

Chemical Preparation

3-Methyl-1-butene is obtained by dehydration of isoamyl alcohol and by dehydrobromination of isoamyl bromide with alcoholic potassium hydroxide.

Chemical Properties

3-Methyl-1-butene undergoes typical olefin reactions. For representative reactions see chemical properties of 1-butene.

Thermodynamic and Detailed Physical Data

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous 3-methyl-1-butene.

Vapor Pressure (2)

The vapor pressure of liquid 3-methyl-1-butene between 273.368 °K and 324.289 °K is shown below:

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
273.368	47.36	473.6	355.25
278.262	57.80	578.0	433.53
283.203	70.11	701.1	525.86
288.183	84.52	845.2	633.94
293.211	101.325	1 013.25	760.00
298.278	120.8	1 208	906.00
303.395	143.3	1 433	1 074.6
308.552	169.1	1 691	1 268.1
313.752	198.5	1 985	1 489.2
318.997	232.1	2 321	1 740.7
324.289	270.1	2 701	2 025.9

The above vapor pressure data are represented by the Antoine vapor pressure equation

$$\log_{10} p = A - \frac{B}{C + t}$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.826 18, 1 013.74, and 236.816, respectively.

For additional vapor pressure data, see vapor pressure curve (Figure 3).

Latent Heat of Vaporization, ΔHv

Temperature, °C	ΔHv, kJ/kg
−20	372.2
0	356.7
20.1	343.0

Thermodynamic Properties of 3-Methyl-1-butene As Ideal Gas @ 25 °C (3)

Heat Capacity, C_p°	118.616 J/(mol·°K)
Entropy, S°	333.465 J/(mol·°K)
Enthalpy of Formation, H_f°	−28.953 kJ/mol
Free Energy of Formation, F_f°	73.889 kJ/mol
Enthalpy of Formation, Liquid @ 25 °C	−53.388 kJ/mol
Free Energy of Formation, Liquid @ 25 °C	74.308 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of 3-methyl-1-butene, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] D. W. Scott and G. Waddington, *J. Amer. Chem. Soc.* 72, 4310–4311 (1950).

[3] C. E. Miller and F. D. Rossini, *Physical Constants of Hydrocarbons, C_1 to C_{10}, 1961*, American Petroleum Institute, New York, New York.

[4] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

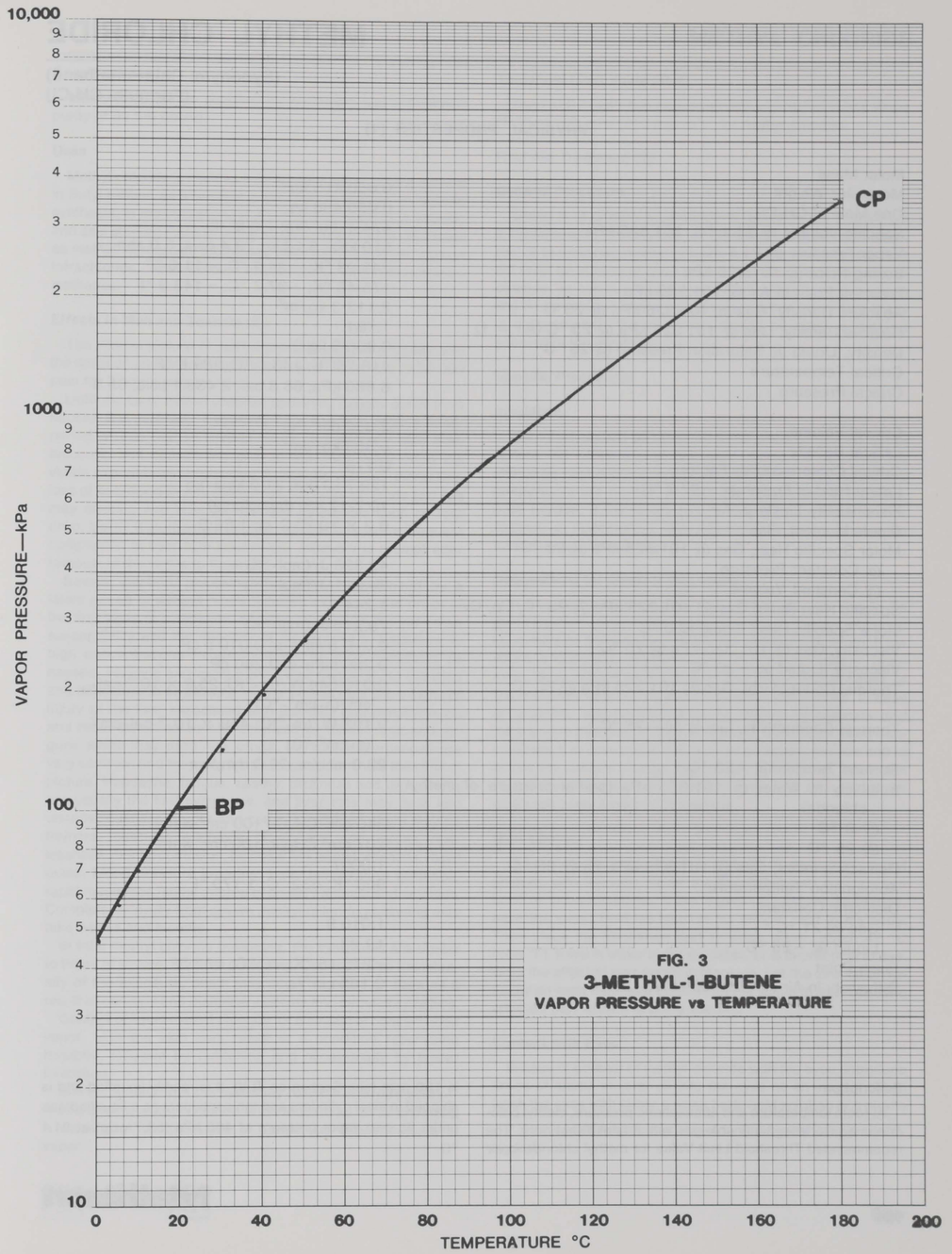


FIG. 3
3-METHYL-1-BUTENE
VAPOR PRESSURE vs TEMPERATURE

METHYL CHLORIDE

(Synonym: Chloromethane)
(Formula: CH_3Cl)

PHYSICAL PROPERTIES (1)

Molar Mass	0.050 488 kg
Molecular Weight	0.050 488 kg
One Mole of CH_3Cl	474.4 dm^3/kg; 7.6 ft^3/lb
Specific Volume @ 21.1 °C, 101.325 kPa	510 kPa, 5.1 bar; 73.4 psia; 5.0 atm
Vapor Pressure @ 21.1 °C	248.93 °K; −24.2 °C; −11.6 °F
Boiling Point @ 101.325 kPa	175.43 °K; −97.7 °C; −143.9 °F
Freezing Point In Air @ 101.325 kPa	2.113 3 kg/m^3
Absolute Density, Gas @ 101.325 kPa @ 25°C	1.784
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	0.906 5 kg/l
Density, Liquid @ Saturation Pressure @ 25 °C	416.25 °K; 143.1 °C; 289.6 °F
Critical Temperature	6 680 kPa; 66.8 bar; 2 438.1 psia; 65.9 atm
Critical Pressure	2.832 dm^3/kg
Critical Volume	0.353 kg/dm^3
Critical Density	0.276
Critical Compressibility Factor	129.7 kJ/kg; 31.0 kcal/kg
Latent Heat of Fusion @ −97.7 °C	10.7-17.4% (by volume)
Flammability Limits In Air	6.2×10^{-30} C·m; 1.86 D
Dipole Moment, Gas	
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	42.326 J/(mol·°K)
@ Constant Volume	34.011 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.244
Molar Specific Heat, Liquid @ 0 °C	79.216 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.010 8 mPa·s; 0.010 8 cP
Viscosity, Liquid @ −20 °C	0.280 mPa·s; 0.280 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 20 °C	0.010 544 W/(m·°K); 25.2×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −25 °C	0.192 W/(m·°K); 459×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −20 °C	22.0 mN/m; 22.0 dyn/cm
Solubility In Water @ 101.325 kPa (partial pressure of methyl chloride)	
@ 0 °C	340 cm^3 CH_3Cl/100 cm^3 water
@ 25 °C	207 cm^3 CH_3Cl/100 cm^3 water
Refractive Index, Gas @ 101.325 kPa, n_D @ 25 °C	1.0007
Autoignition Temperature	905 °K; 632 °C; 1 170 °F
Dielectric Constant	
Gas @ 21 °C	1.010 9
Liquid @ −25 °C	12.93
Flash Point	<273.15 °K; <0 °C; <32 °F
Diffusivity In Air @ 101.325 kPa @ 25 °C	0.105 cm^2/s

Description

At room temperature and atmospheric pressure, methyl chloride is a colorless, flammable gas with a faint sweet odor. The recommended Threshold Limit Value for methyl chloride in air is 100 ppm (see Section on TLV). It is readily liquefied and is shipped in steel cylinders and ton containers as a liquefied gas under its own vapor pressure of 405 kPa (58.7 psig) at 21.1 °C.

Specifications

Methyl chloride as supplied by Matheson has a minimum purity of 99.5% (mole).

Uses

Methyl chloride is used as a refrigerant, as a catalyst solvent in Butyl rubber, as a reagent in silicone production, in organic synthesis, in the manufacture of tetramethyllead, as a solvent, and as a starting material in the manufacture of such chemicals as methyl mercaptan, methylene chloride, chloroform, carbon tetrachloride, and various bromochloro- and chlorofluoromethanes.

Effects In Man and Toxicity (2)

The clinical picture of methyl chloride poisoning varies with the duration and intensity of the exposure. Exposure to 20 000 ppm for 2 hours may be fatal.

Light cases of methyl chloride poisoning usually suffer from nausea and vomiting, frequently from anorexia after a latent period of one half to several hours, occasionally also from hiccough and constricting pain in the neck. Very often the victim experiences drowsiness, headache, vertigo, increasing loss of coordination and sleepiness. Tremors of hands and lips may develop and later be followed by paresis such as foot drop. Visual disturbances (sich as double vision) are frequent complaints. In very light poisonings, recovery is prompt after removal of the victim to fresh air.

Severe, nonfatal poisonings are also characterized by a latent period of several hours between exposure and onset of the first signs or symptoms, and this varies with the individual susceptibility and the intensity of the exposure. Exposure to high concentrations frequently leads to such symptoms as nausea, vomiting and colicky pain, less frequently to diarrhea and difficulties in swallowing. Some victims may show signs of injury of the liver associated with jaundice and porphyrinuria and renal disturbances characterized by albuminuria and oliguria which may pass into anuria. Nervous disturbances are very common and they may be severe and dominate the clinical picture. Headache, fatigue, apathy, dizziness and drowsiness are usually the first symptoms, and later they may pass into unconsciousness, stupor and coma. In addition, there may be tremors, muscular twitchings, clonic-tonic convulsions, restlessness, mental confusion, halitosis, visual disturbances, rapid pulse, blood pressure lowering, body temperature elevation, rapid respiration, some degree of primary anemia and acidosis. Complete recovery from severe methyl chloride poisoning may take weeks and months.

In fatal methyl chloride poisoning, the symptoms are similar to those of severe, nonfatal poisoning. Depending on the intensity of the exposure, death may occur in hours or days as a result of cerebral and pulmonary edema and circulatory failure.

Contact of liquid methyl chloride, or a stream of concentrated vapor, with the skin may result in a condition resembling frostbite, followed by reddening and occasionally by blister formation.

Similar contact with the eyes may result in a severe injury.

The odor of methyl chloride is inadequate as far as providing a warning of the presence of dangerous concentrations of vapor.

Threshold Limit Value (TLV)

The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 100 ppm (210 mg/m^3)* for methyl chloride.

First Aid Treatment (2)

General Procedure

Speed is of primary importance in removing the victim from a contaminated atmosphere, in removing contaminated clothing, or in removing methyl chloride from the skin of eyes. First aid must be started at once in all cases of contact with methyl chloride as serious injury may result. All affected persons should be referred to a physician, even when immediate injury is not apparent. The physician should be given a detailed account of the accident.

Specific Procedures

Inhalation

The victim should be removed to an uncontaminated atmosphere. All contaminated garments should be removed. He should be kept and comfortably warm until blood pressure and temperature are normal. In case the respiration is impaired, pure oxygen, if necessary (when respiration is weak or has ceased) in combination with artificial respiration, should be administered periodically.

Suggestions for Medical Treatment

In case of incipient pulmonary edema, oxygen should be given against a positive pressure of 3–4 cm of water, obtained by immersing the exhalation tube into water to this depth. If the victim is comatose, analeptics may become necessary. However, these should be given with due precaution because of the tendency of some victims to develop convulsions. In case of acidosis, oral administration of sodium bicarbonate and intravenous injection of its 5% solution have been used successfully. It is essential to maintain an adequate diuresis and to empty the urinary bladder periodically. Otherwise, the victim should be maintained on a high protein diet and should be given adequate amounts of vitamins.

Skin Contact

In case frostbite develops as a result of contact of methyl chloride with the skin, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation reestablish itself naturally. Encourage the victim to excercise the affected part while it is being warmed.

Contact with Eyes

In case of contact of methyl chloride with the eyes, introduce drops of sterile mineral oil into the eyes as an irrigant. Then wash the eyes with either a weak boric acid solution or a sterile

* 1979 ACGIH Notice of Intent to Change to 50 ppm (105 mg/m^3).

salt solution, not to exceed 2% sodium chloride. Take the victim promptly to an eye specialist.

Precautions in Handling and Storage

All personnel handling methyl chloride cylinders should be fully informed as to the dangers incident to improper handling. The cylinder and system should be grounded before use. Before introducing methyl chloride into any apparatus or equipment, this apparatus should be tested for leaks, all leaks repaired, and the apparatus thoroughly dried. Only non-sparking tools should be used with methyl chloride. Chemical safety goggles and/or a full face shield should be used when handling liquid methyl chloride. Where there is danger of high concentrations of methyl chloride, the operator should wear an approved (NIOSH) air or oxygen supplied mask, with a full face piece and have it ready for emergencies. Spills, unless very large, usually evaporate rapidly and cause little damage, but ample ventilation should be provided to prevent the formation of toxic and explosive mixtures. Leaking cylinders should be moved outdoors, or to an isolated, well-ventilated area where the contents may be released. Each employee should know the location of safety showers, eye-fountains, and fire-extinguishing equipment. Use methyl chloride in a well-ventilated area only, preferably a hood with forced ventilation. The cylinder should never be directly connected to a container of liquid, since suckback can occur causing a reaction within the cylinder. To prevent suckback a trap, checkvalve, or vacuum break should be inserted into the line. Because of the fire and explosion hazards, cylinders of methyl chloride should be stored and used only in well-ventilated areas away from heat and all sources of ignition such as flames and sparks. Never use flames to detect methyl chloride leaks, use soapy water solution. Do not use methyl chloride around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of methyl chloride cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Never use a flame to detect leaks of methyl chloride. Leaks in equipment to contain methyl chloride are best detected by placing the unit under nitrogen or carbon dioxide pressure and applying soap solution to the suspected points; during freezing weather glycerine may be used. A leak will be shown by the formation of bubbles. Methyl chloride concentrations in air may be determined with an explosimeter.

Disposal of Leaking Cylinders

Methyl chloride may be absorbed from leaking cylinders in a suitable organic solvent such as xylene, toluene, benzene, or chloroform after attachment of the appropriate regulator and flexible tubing and subsequently recovered for use or it may be disposed of by the procedure described in Appendix II-A.

Materials of Construction

Dry methyl chloride is inert to most engineering materials except zinc, aluminium die castings, and possibly magnesium alloys. It is particularly important to avoid the use of aluminum in contact with methyl chloride, since dangerous spontaneously flammable methyl aluminum compounds may be formed. In the presence of moisture, methyl chloride hydrolyzes with the formation of corrosive hydrochloric acid. Gaskets composed of natural rubber and many of the neoprene compositions are not suitable for use with methyl chloride. Pressed fibers, including asbestos, with a number of insoluble binders such as glue and gums, may be used. Polyvinyl alcohol gaskets, tubing, valve seats, and washers are recommended for use with methyl chloride. Medium soft metal gaskets may be used where alternating stresses do not produce "ironing out" with subsequent leakage.

Cylinder and Valve Description

Cylinders of methyl chloride are of the low pressure type having a rated service pressure of 1 034 kPa (150 psig) or more.

The standard cylinder valve outlet for methyl chloride is Compressed Gas Association (CGA) connection No. 510. Matheson has adopted connection No. 660 for methyl chloride service. This valve outlet is 1.030 inches in diameter, with right-hand external threads, but is used with a connection having a flat seat and washer (see Figure 1 for an illustration of this valve outlet and its mating connection). Lecture bottles have a special 5/16"-32 threads per inch female valve outlet.

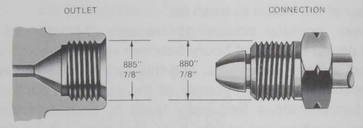


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat Washer

Safety Devices

Cylinders of methyl chloride utilize safety devices consisting of fuse plugs, melting at about 73.9 °C (165 °F). When the cylinder is over 30 inches long, exclusive of the neck, this device is used in both ends of the cylinder.

Recommended Controls

Automatic Regulators

Single stage metal diaphragm regulator, Model 19C-660 is recommended for use with methyl chloride. The regulator is of all brass construction, with German silver alloy diaphragm, nylon seat, and aluminum and nylon gaskets. It has a delivery pressure range of 28–345 kPa (4–50 psig), and a 2½" delivery pressure gauge reading up to 690 kPa (100 psig). Regulator Model 3321 with a delivery pressure range of 28–410 kPa (4–60 psig) is recommended for use with lecture bottles.

Manual Controls

Matheson needle valve Model 50-660, a brass bar stock valve, is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a hose connection, ¼" tube fitting, or ¼" NPT male or female pipe. It should be used only for manual flow control and not as a pressure control since it will not prevent pressure from building up if the system becomes clogged or if the system itself is closed. A Model 31B manual needle valve can be supplied for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Methyl chloride is classified by the DOT as a flammable, compressed gas and is shipped with the required "Red Gas Label".

Commercial Preparation

Methyl chloride is obtained by the chlorination of methane in light along with other chlorination products. The proportion of methyl chloride formed depends on the reaction conditions. It is also produced by treating methanol with hydrogen chloride in the presence of dehydrating agents.

Chemical Properties

Methyl chloride undergoes the following typical reactions.

(a) Forms a Grignard reagent with magnesium.

(b) Methylates aromatic hydrocarbons with aluminum chloride as a catalyst.

(c) Reacts with alkali alkoxides giving ethers (Williamson).

(d) Forms quaternary salts with tertiary amines.

(e) Reacts with ammonia forming methylamines.

(f) Methylates amines in the presence of hydrogen chloride acceptors.

(g) Reacts with the sodium salts of organic acids to form methyl esters.

In addition, methyl chloride undergoes numerous other nucleophilic displacement reactions.

Thermodynamic and Detailed Physical Data

Molecular Structure

Replacement of one of the hydrogens of methane by chlorine results in distortion of the original tetrahedral symmetry of the methane molecule. Because of the electronegative character of the chlorine atom, methyl chloride has a permanent dipole moment with the chlorine atom the negative end of the dipole. The dipole moment of the polar methyl chloride molecule is 1.86 debye units. Methane which is a symmetrical molecule has no permanent dipole moment.

The methyl chloride molecule has C_{3v} symmetry and a symmetry number of three, with C—H and C—Cl bond distances of 1.095 9 Å ($1.095\ 9 \times 10^{-10}$ m) and 1.781 Å ($1.781\ 2 \times 10^{-10}$ m), respectively, and H—C—H and H—C—Cl bond angles of 108° and 110.9°, respectively.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous methyl chloride.

Vapor Pressure (3)

The vapor pressure of liquid methyl chloride is represented by the Antoine vapor pressure equation

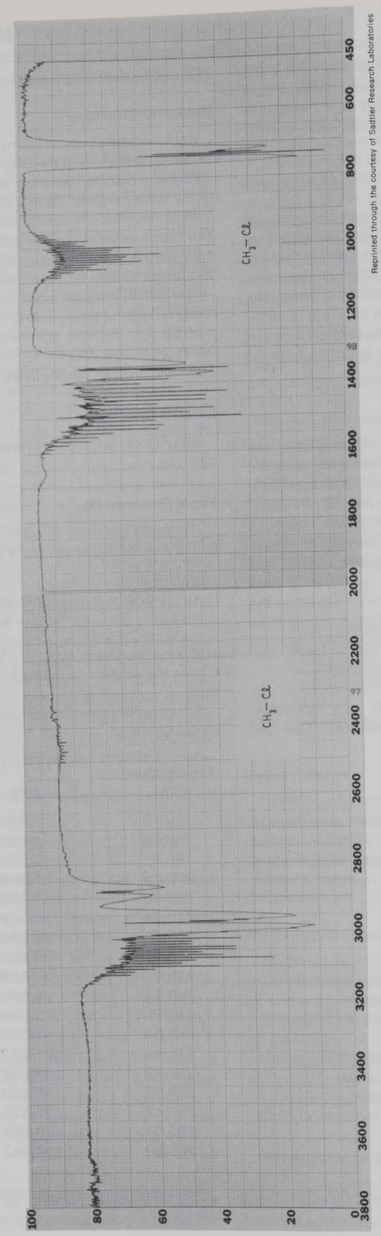
$$\log_{10} p = A - \frac{B}{C + t} \quad \text{or} \quad t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.994 45, 902.451, and 243.60, respectively.

Some vapor pressure values calculated by this equation are shown below:

Temperature,	Vapor Pressure		
°K	kPa	mbar	mmHg
180.10	1.333	13.3	10
188.06	2.666	26.7	20
196.91	5.333	53.3	40
202.55	7.999	80.0	60
206.80	10.666	106.7	80
210.24	13.332	133.3	100
221.83	26.664	266.6	200
229.32	39.997	400.0	300
235.01	53.329	533.3	400
239.64	66.661	666.6	500
243.59	79.993	799.9	600
247.04	93.325	933.2	700
248.93	101.325	1 013.25	760
250.12	106.658	1 067	800
252.92	119.990	1 200	900
255.48	133.322	1 333	1 000
260.04	159.986	1 600	1 200
265.89	199.983	2 000	1 500

For vapor pressures at higher temperatures, see Table 2 and Figure 3.



©Sadtler 1972

Reprinted through the courtesy of Sadtler Research Laboratories

Fig. 2. Infrared spectrum of gaseous methyl chloride over the frequency range of 3 800 cm^{-1} to 450 cm^{-1}; 10 cm path length cell, with KBr optics; cell pressure (complete scan): 12.0 kPa (90 mmHg) (5).

Latent Heat of Vaporization, ΔHv @ 248.93°K 428.44 kJ/kg; (184.3 Btu/lb; 102.4 kcal/kg)

For ΔHv values at other temperatures, see Table 2.

Thermodynamic Data

Thermodynamic properties of methyl chloride for the saturated liquid and the superheated vapor are shown in Tables 2 and 3, respectively. Compressibility data are shown in Table 1.

Thermodynamic Properties of Methyl Chloride As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p^o	40.694 J/(mol·°K)
Entropy, S_o	234.250 J/(mol·°K)
Free Energy Function, $(F_{298}^o - H_{298}^o)/298$	−234.250 J/(mol·°K)

TABLE 1. COMPRESSIBILITY FACTORS FOR METHYL CHLORIDE

Temperature, °K	Pressure, kPa				
	101.325	1 013.25	2 026.50	4 053.000	6 079.50
273.15	0.989				
298.15	0.990				
400	0.995	0.939	0.871	0.705	
500	0.998	0.974	0.947	0.896	0.820
600	0.999	0.989	0.975	0.944	0.919
800	1.000	0.993	0.992	0.987	0.985
1 000	1.000	0.997	0.996	0.995	0.994

Enthalpy Difference, $H_{298}^o - H_o^o$	10.414 kJ/mol
Enthalpy of Formation, ΔH_f^o	−86.441 kJ/mol
Free Energy of Formation, ΔF_f^o	−62.952 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of methyl chloride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 97–100, Matheson, Lyndhurst, New Jersey.

[3] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds*, *1968*, Volume 1, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[4] *JANAF Thermochemical Tables*, 2nd edition, D. R. Stull and H. Prophet, project directors, *1971*, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[5] *The Sadtler Standard Spectra*, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[6] *Methyl Chloride*, Tech. Bull. *1947*, pp. 23–24, E. I. duPont de Nemours & Co., Wilmington, Delaware.

[7] *Ibid.*, pp. 25–30.

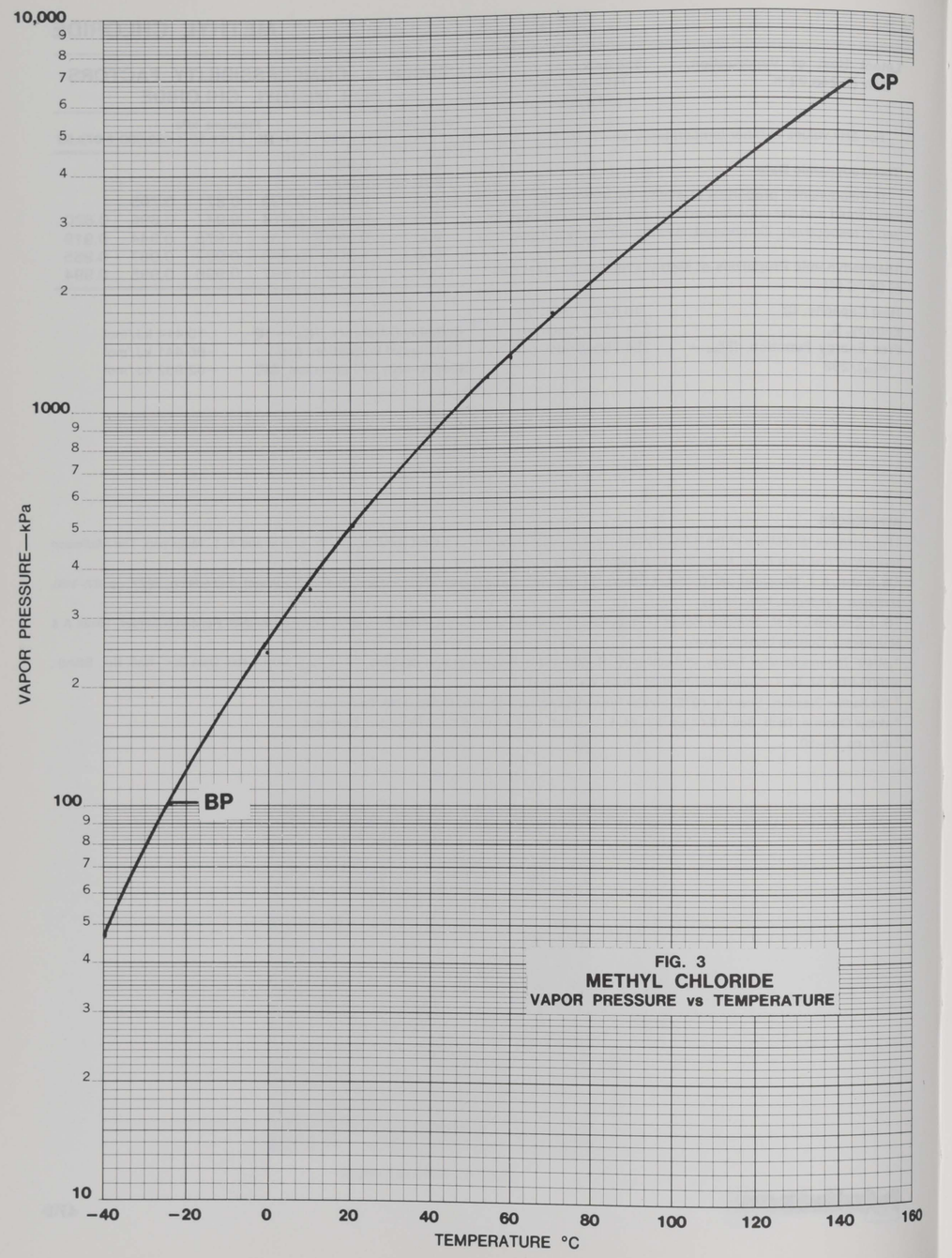


FIG. 3
METHYL CHLORIDE
VAPOR PRESSURE vs TEMPERATURE

Table 2. THERMODYNAMIC PROPERTIES OF SATURATED METHYL CHLORIDE (6)

Temperature		Pressure		Entropy kJ/(kg·°K)		Enthalpy kJ/kg		Latent Heat of Vaporization kJ/kg	Specific Volume m^3/kg		Density kg/m^3	
°K	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
210.93	−80	13.465	0.133	−0.147	2.043	−32.282	429.441	461.723	0.000 932	2.564 5	1 073.0	0.389 9
216.48	−70	18.967	0.187	−0.109	2.004	−24.455	432.928	457.383	0.000 941	1.862 9	1 062.7	0.536 8
222.04	−60	26.193	0.259	−0.072	1.968	−16.362	436.391	452.753	0.000 951	1.379 0	1 051.5	0.725 2
227.59	−50	35.542	0.351	−0.036	1.933	−8.210	439.762	447.972	0.000 960	1.038 8	1 041.7	0.962 6
233.15	−40	47.422	0.468	0.000	1.901	0.000	443.178	443.178	0.000 970	0.794 1	1 030.9	1.259
238.71	−30	62.301	0.615	0.035	1.871	8.280	446.479	438.199	0.000 979	0.616 4	1 021.5	1.622
244.26	−20	80.738	0.797	0.069	1.843	16.610	449.757	433.147	0.000 988	0.484 5	1 012.1	2.064
249.82	−10	103.146	1.02	0.103	1.817	24.988	452.964	427.976	0.000 998	0.385 6	1 002.0	2.593
255.37	0	130.311	1.29	0.137	1.792	33.449	456.126	422.677	0.001 007	0.310 2	993.0	3.224
260.93	10	162.716	1.61	0.170	1.769	41.933	459.264	417.331	0.001 018	0.252 1	982.3	3.967
266.48	20	201.051	1.98	0.203	1.748	50.510	462.192	411.682	0.001 028	0.206 8	972.8	4.836
272.04	30	246.005	2.43	0.234	1.726	59.134	464.959	405.825	0.001 039	0.171 0	962.5	5.848
277.59	40	298.198	2.94	0.266	1.707	67.804	467.608	399.804	0.001 051	0.142 7	951.5	7.008
283.15	50	358.458	3.54	0.297	1.688	76.544	470.189	393.645	0.001 064	0.119 9	939.8	8.340
288.71	60	427.475	4.22	0.328	1.670	85.330	472.629	387.299	0.001 076	0.101 4	929.4	9.862
294.26	70	506.144	5.00	0.358	1.653	94.186	474.977	380.791	0.001 089	0.086 3	918.3	11.587
299.82	80	594.742	5.87	0.388	1.636	103.112	477.139	374.027	0.001 101	0.073 9	908.3	13.532
305.37	90	693.612	6.85	0.418	1.620	112.061	479.138	367.077	0.001 115	0.063 6	896.9	15.723
310.93	100	804.618	7.94	0.447	1.605	121.080	481.020	359.940	0.001 129	0.055 0	885.7	18.182
316.48	110	927.345	9.15	0.476	1.590	130.169	482.787	352.618	0.001 144	0.047 9	874.1	20.877
322.04	120	1 063.17	10.5	0.505	1.577	139.304	484.391	345.087	0.001 161	0.041 9	861.3	23.866
327.59	130	1 212.79	12.0	0.533	1.563	148.509	485.855	337.346	0.001 172	0.036 8	853.2	27.174
333.15	140	1 376.19	13.6	0.561	1.550	157.760	487.157	329.397	0.001 195	0.032 4	836.8	30.864
338.71	150	1 554.08	15.3	0.589	1.537	167.058	488.366	321.308	0.001 214	0.028 6	823.7	34.965
344.26	160	1 747.82	17.2	0.616	1.525	176.425	489.435	313.010	0.001 235	0.025 4	809.7	39.370
349.82	170	1 957.42	19.3	0.643	1.514	185.886	490.295	304.409	0.001 258	0.022 6	794.9	44.248

Table 3. THERMODYNAMIC PROPERTIES SUPERHEATED METHYL CHLORIDE (7)

Pressure kPa	Pressure atm		Temper 255.37	266.48	277.59	288.71	299.82	310.93	322.04	333.15	344.26	355.37
41,369	0.408	H	459.868	468.329	476.953	485.832	494.828	503.986	513.330	522.860	532.553	542.432
		S	1.992	2.024	2.056	2.087	2.118	2.148	2.177	2.207	2.235	2.264
		V	1.004 5	1.050 0	1.095 6	1.140 6	1.185 5	1.230 5	1.274 8	1.319 7	1.364 7	1.409 0
69.948	1.021	H	458.659	467.306	476.000	484.926	494.014	503.242	512.633	522.233	531.972	541.898
		S	1.905	1.937	1.969	2.001	2.032	2.062	2.092	2.121	2.150	2.178
		V	0.597 2	0.624 9	0.652 4	0.679 8	0.707 3	0.734 5	0.762 2	0.789 7	0.816 6	0.884 0
103,421	1.021	H	457.148	466.005	474.837	483.810	492.991	502.289	511.733	521.443	531.252	541.247
		S	1.834	1.867	1.900	1.931	1.963	1.993	2.023	2.053	2.082	2.110
		V	0.394 1	0.413 1	0.431 8	0.450 4	0.471 4	0.487 3	0.050 7	0.524 0	0.542 2	0.560 5
137,895	1.361	H		464.656	473.605	482.694	491.969	501.359	510.913	520.652	530.531	540.573
		S		1.816	1.849	1.881	1.913	1.943	1.974	2.003	2.033	2.061
		V		0.307 0	0.321 3	0.335 4	0.349 5	0.363 5	0.377 4	0.391 3	0.405 1	0.418 8
206,843	2.041	H			470.979	480.463	489.923	499.453	509.193	519.048	529.067	539.201
		S			1.776	1.809	1.841	1.872	1.903	1.933	1.963	1.992
		V			0.210 6	0.220 4	0.230 2	0.239 7	0.249 2	0.275 4	0.267 9	0.277 3
275.790	2.722	H			468.097	478.115	487.761	497.501	507.473	517.421	527.556	537.830
		S			1.722	1.756	1.789	1.820	1.852	1.882	1.912	1.942
		V			0.155 1	0.162 8	0.170 4	0.177 7	0.185 0	0.192 3	0.199 5	0.206 6
413.685	4.083	H				473.001	483.298	493.479	503.684	514.074	524.534	535.064
		S				1.677	1.711	1.744	1.777	1.808	1.839	1.869
		V				0.105 1	0.110 5	0.115 7	0.120 9	0.125 9	0.130 9	0.135 8
551.581	5.444	H					478.487	489.295	499.802	510.634	521.419	532.205
		S					1.652	1.687	1.721	1.754	1.785	1.816
		V					0.080 5	0.084 7	0.088 7	0.092 7	0.096 6	0.100 4
689.476	6.805	H						484.833	495.874	507.077	518.212	529.299
		S						1.640	1.675	1.709	1.742	1.774
		V						0.065 9	0.069 4	0.072 7	0.076 0	0.079 2
827.371	8.166	H							491.876	503.405	514.888	526.301
		S							1.636	1.671	1.705	1.737
		V							0.056 4	0.059 4	0.062 2	0.065 0
965.266	9.526	H							487.436	499.616	511.475	523.209
		S							1.600	1.636	1.672	1.705
		V							0.047 1	0.049 7	0.052 3	0.054 7
1 103.15	10.89	H								495.664	507.891	520.048
		S								1.605	1.642	1.677
		V								0.042 5	0.044 9	0.047 1
1 241.06	12.25	H								491.434	504.218	516.770
		S								1.577	1.614	1.650
		V								0.036 8	0.039 1	0.041 1
1 378.95	13.61	H									500.453	513.400
		S									1.588	1.626
		V									0.034 4	0.036 3
1 516.84	14.97	H									496.501	509.937
		S									1.564	1.603
		V									0.030 5	0.032 4
1 654.74	16.33	H									492.201	506.310
		S									1.541	1.581
		V									0.027 3	0.029 1
1 792.64	17.69	H										502.498
		S										1.560
		V										0.026 3

H, ENTHALPY, kJ/kg; **S**, ENTROPY, kJ/(kg·°K); **V**, SPECIFIC VOLUME, m^3/kg

ature, °K 366.48	377.59	388.71	399.82	410.93	422.04	433.15	444.26	455.37	466.48	477.59	488.71	499.82
552.497	562.725	573.208	583.74									
2.291	2.319	2.346	2.373									
1.453 9	1.498 3	1.542 6	1.586 9									
551.986	562.260	572.789	583.389	594.267								
2.206	2.234	2.261	2.288	2.315								
0.870 9	0.897 7	0.924 6	0.951 4	0.978 2								
551.381	561.679	572.255	582.901	593.779	604.727							
2.138	2.166	2.193	2.220	2.247	2.274							
0.578 6	0.596 6	0.614 5	0.632 4	0.650 5	0.668 6							
550.754	561.121	571.720	582.389	593.268	604.262							
2.089	2.118	2.145	2.172	2.199	2.225							
0.432 6	0.446 2	0.459 8	0.473 4	0.487 0	0.506 2							
549.499	559.959	570.651	581.413	592.315	603.379	614.606						
2.020	2.048	2.076	2.104	2.130	2.157	2.183						
0.286 6	0.295 8	0.305 1	0.314 3	0.323 4	0.332 5	0.341 6						
548.243	558.796	569.582	580.414	591.385	602.519	613.793	625.275					
1.971	1.999	2.027	2.054	2.081	2.108	2.135	2.161					
0.213 7	0.220 7	0.227 7	0.234 7	0.241 5	0.248 4	0.255 3	0.262 1					
545.710	556.472	567.420	578.391	589.502	600.776	612.142	623.672					
1.899	1.928	1.956	1.984	2.012	2.038	2.065	2.092					
0.140 7	0.145 5	0.150 3	0.155 0	0.159 8	0.164 4	0.169 1	0.173 7					
543.106	554.078	565.212	576.346	587.596	598.986	610.492	622.114	633.876	645.870			
1.846	1.876	1.905	1.933	1.961	1.988	2.015	2.041	2.068	2.094			
0.104 1	0.107 9	0.111 6	0.115 2	0.118 9	0.122 4	0.125 9	0.129 4	0.132 9	0.136 4			
540.433	551.637	562.980	574.277	585.667	597.196	608.842	620.557	632.411	644.452			
1.804	1.834	1.864	1.892	1.921	1.948	1.976	2.002	2.029	2.055			
0.082 3	0.085 3	0.088 3	0.091 3	0.094 3	0.097 2	0.100 1	0.102 9	0.105 8	0.108 6			
537.714	549.150	560.702	572.185	583.714	595.406	607.145	618.976	630.947	643.011	655.191		
1.769	1.800	1.830	1.859	1.887	1.915	1.943	1.970	1.996	2.023	2.048		
0.067 6	0.070 2	0.072 9	0.075 4	0.077 8	0.080 3	0.082 8	0.085 2	0.087 6	0.090 0	0.092 3		
534.924	546.639	558.401	570.047	581.762	593.570	605.425	617.396	629.459	641.593	653.866	666.441	
1.738	1.769	1.800	1.830	1.859	1.887	1.915	1.942	1.969	1.995	2.021	2.047	
0.057 1	0.059 5	0.061 7	0.063 9	0.066 2	0.068 3	0.070 4	0.072 5	0.074 7	0.076 8	0.078 9	0.080 9	
532.065	544.036	556.030	567.862	579.763	591.710	603.705	615.792	627.949	640.198	652.541	665.163	
1.710	1.742	1.774	1.804	1.833	1.861	1.889	1.917	1.944	1.971	1.997	2.023	
0.049 3	0.051 4	0.053 4	0.055 4	0.057 4	0.059 3	0.061 2	0.063 1	0.064 9	0.066 8	0.068 8	0.070 4	
529.136	541.409	553.613	565.677	577.717	589.828	601.961	614.165	626.438	638.757	651.193	663.861	
1.685	1.718	1.750	1.780	1.810	1.839	1.867	1.895	1.923	1.949	1.976	2.002	
0.043 1	0.045 1	0.046 9	0.048 8	0.050 5	0.052 3	0.054 0	0.055 7	0.057 4	0.059 1	0.060 7	0.062 4	
526.138	538.690	551.172	563.422	576.649	587.922	600.195	612.514	624.904	637.339	649.891	662.583	
1.661	1.695	1.728	1.759	1.789	1.818	1.818	1.847	1.875	1.902	1.930	1.956	
0.038 2	0.040 0	0.041 7	0.043 4	0.045 0	0.046 6	0.048 2	0.049 8	0.051 3	0.052 9	0.054 3	0.055 9	
523.046	535.924	548.639	561.120	573.533	585.992	598.428	610.864	623.346	635.875	648.497	661.304	674.089
1.639	1.674	1.707	1.739	1.770	1.800	1.828	1.857	1.884	1.912	1.938	1.965	1.991
0.034 1	0.035 8	0.037 5	0.039 0	0.040 6	0.042 1	0.043 5	0.044 9	0.046 4	0.047 8	0.049 1	0.050 6	0.051 9
519.839	533.065	546.082	558.796	571.395	584.040	596.615	609.190	621.789	634.434	647.125	660.003	672.880
1.618	1.654	1.688	1.720	1.751	1.782	1.811	1.840	1.868	1.895	1.922	1.949	1.975
0.030 8	0.032 4	0.033 9	0.035 3	0.036 8	0.038 2	0.039 6	0.040 9	0.042 3	0.043 5	0.044 8	0.046 1	0.047 3
516.540	530.159	543.478	556.425	569.256	582.064	594.802	607.493	620.208	632.969	645.731	658.724	671.671
1.598	1.635	1.670	1.703	1.734	1.765	1.795	1.824	1.852	1.880	1.907	1.933	1.960
0.027 9	0.029 4	0.030 9	0.032 3	0.033 6	0.035 0	0.036 3	0.037 5	0.038 8	0.040 0	0.041 1	0.042 4	0.043 5

METHYL FLUORIDE

(Synonym: Fluoromethane)
(Formula: CH_3F)

PHYSICAL PROPERTIES (1)

Molar Mass	0.034 033 kg
Molecular Weight	0.034 033 kg
One Mole of CH_3F	709.2 dm^3/kg; 11.36 ft^3/lb
Specific Volume @ 21.1 °C, 101.325 kPa	3 810 kPa; 38.1 bar; 552.7 psia; 37.6 atm
Vapor Pressure @ 21.1 °C	194.80 °K; −78.4 °C; −109.0 °F
Boiling Point @ 101.325 kPa	131.35 °K; −141.8 °C; −223.2 °F
Freezing Point In Air @ 101.325 kPa	1.439 7 kg/m^3
Absolute Density, Gas @ 101.325 kPa @ 20°C	1.195
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	0.557 0 kg/l
Density, Liquid @ Saturation Pressure @ 25 °C	318.05 °K; 44.9 °C; 112.8 °F
Critical Temperature	6 280 kPa; 62.8 bar; 911.1 psia; 62.0 atm
Critical Pressure	3.320 dm^3/kg
Critical Volume	0.301 kg/dm^3
Critical Density	0.268
Critical Compressibility Factor	6.174×10^{-30} C·m; 1.851 D
Dipole Moment, Gas	
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	38.171 J/(mol·°K)
@ Constant Volume	29.857 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.278
Viscosity, Gas @ 101.325 kPa @ 25°C	0.010 86 mPa·s; 0.010 86 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.016 99 W/(m·°K); 40.6×10^{-6} cal·cm/(s·cm^2·°C)
Solubility In Water @ 101.325 kPa @ 15 °C	166 cm^3 CH_3F/0.1 kg
Refractive Index, Liquid @ Saturation Pressure @ 25 °C	1.167 4

Description

Methyl fluoride is a colorless, flammable gas at room temperature and atmospheric pressure. Methyl fluoride is shipped only in lecture bottles as a liquefied gas under its own vapor pressure of 3 710 kPa (538 psig) at 21.1 °C.

Specifications

Methyl fluoride as supplied by Matheson has a minimum purity of 99.0%.

Uses

Methyl fluoride is chiefly of interest as a propellant in admixture with other nonflammable propellants and for physicochemical study of the C—F bond.

Toxicity

The toxicity of methyl fluoride has not been investigated, but it is probably of a lower order. Nevertheless, it is advisable to handle it in a well-ventilated area.

Precautions in Handling and Storage

The hazards associated with the use of methyl fluoride stem mainly from its flammability. Store and use methyl fluoride cylinders in well-ventilated areas away from heat and all sources of ignition such as flames and sparks. Never use flames to detect flammable gas leaks, use soapy water. Do not use methyl fluoride around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of methyl fluoride cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all lines used with methyl fluoride.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks of methyl fluoride in lines or equipment may be detected by painting the suspected sites with soapy water. Leaks will be indicated by bubble formation. Never use a flame to detect leaks.

Matheson

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-A.

Materials of Construction

Since methyl fluoride is a noncorrosive gas, any common or commercially available metal may be used. However, piping systems or vessels to contain methyl fluoride should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

Methyl fluoride is supplied in lecture bottles, which have a special 5/16"-32 threads per inch female outlet.

Recommended Controls

Automatic Regulators

Regulator Models 3320 and 3321 which are designed for use with lecture bottles containing noncorrosive gases are recommended for use with methyl fluoride. These regulators are of brass construction with neoprene diaphragms and Kel-F seats. Both regulators have delivery pressure ranges of 28–410 kPa (4–60 psig).

Manual Controls

Models 30AR and 31B needle valves are recommended for use with lecture bottles of methyl fluoride.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson series No. 8116 and No. 8160 should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2 %.

Shipping Regulations

Methyl fluoride is shipped in lecture bottles as a flammable compressed gas, requiring a DOT "Red Gas Label".

Chemical Preparation

Methyl fluoride is generally prepared by the interaction of methyl chloride and silver fluoride or mercury fluorides. It is

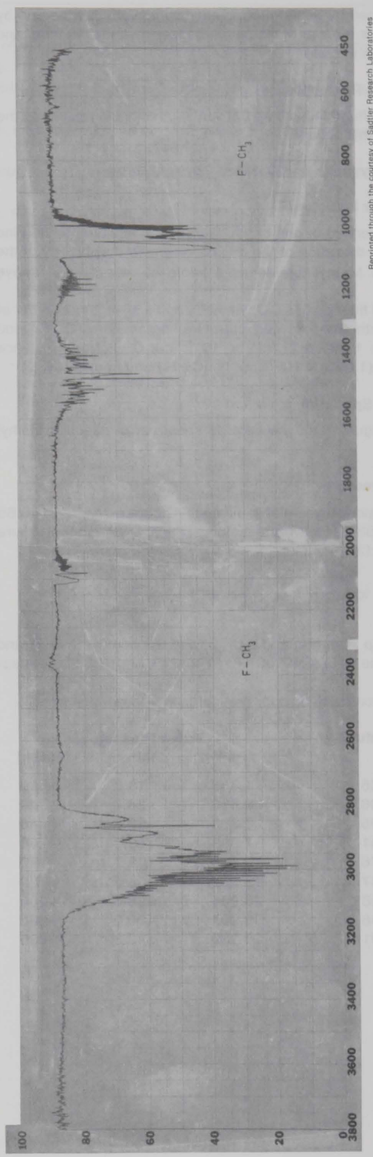


Fig. 1. Infrared spectrum of gaseous methyl fluoride over the frequency range of 3 800 cm^{-1} to 450 cm^{-1}; 10 cm path length cell, with KBr optics; cell pressure (complete scan): 6.666 kPa (50 mmHg) (5).

Matheson

also formed by heating tetramethylammonium fluoride and by refluxing a mixture of methanol, benzenesulfonyl fluoride, and potassium fluoride.

Chemical Properties

Methyl fluoride is comparatively unreactive in relation to the other methyl halides.

Thermodynamic and Detailed Physical Data

Molecular Structure

Replacement of one of the hydrogen in methane by fluorine results in distortion of the original tetrahedral symmetry of the molecule. Methyl fluoride has a dipole moment of 1.851 debye units.

Methyl fluoride has C_{3v} symmetry and a symmetry number of three, with the following structural parameters: C—F bond distance: 1.391 Å (1.391×10^{-10} m); C—H bond distance 1.095 Å (1.095×10^{-10} m); H—C—H bond angle: 109.5°.

Infrared Spectrum

See Figure 1 for the infrared spectrum of gaseous methyl fluoride.

Vapor Pressure

The vapor pressure of liquid methyl fluoride between 140.65 °K and 208.02 °K is represented by the Antoine vapor pressure equation (2).

$$\log_{10} p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 7.097 61, 740.218, and 253.89, respectively.

Some calculated vapor pressures are shown below:

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
140.65	1.333	13.3	10
146.96	2.666	26.7	20
153.95	5.333	53.3	40
158.41	7.999	80.0	60
161.76	10.666	106.7	80
164.47	13.332	133.3	100
173.58	26.664	266.6	200
179.46	39.997	400.0	300
183.91	53.329	533.3	400

Temperature, °K	Vapor Pressure kPa	bar	atm
187.54	66.661	666.6	500
190.63	79.993	799.9	600
193.33	93.326	933.3	700
194.80	101.325	1 013.35	760
195.73	106.658	1 067	800
197.91	119.990	1 200	900
199.91	133.322	1 333	1 000
203.46	159.987	1 600	1 200
208.02	199.984	2 000	1 500

Vapor pressures above 101.325 kPa (1 atm) are shown below (3).

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
194.95	101.325	1.013 25	1
208.65	202.650	2.03	2
231.15	506.625	5.07	5
252.15	1 013.25	10.1	10
275.75	2 026.50	20.3	20
288.65	3 039.75	30.4	30
299.65	4 053.00	40.5	40
309.15	5 066.25	50.7	50
316.65	6 079.50	60.8	60

See Figure 2 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/mol
194.80	17.698
200	17.433
225	15.905

Thermodynamic Properties of Methyl Fluoride As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	37.501 J/(mol·°K)
Entropy, S°	222.806 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−222.806 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	10.134 kJ/mol
Enthalpy of Formation, ΔH_f°	−234.304 kJ/mol
Free Energy of Formation, ΔF_f°	−210.426 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of methyl fluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds, 1968*, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[3] *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p. 3–62, McGraw-Hill Book Co., Inc., New York, New York.

[4] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[5] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Matheson

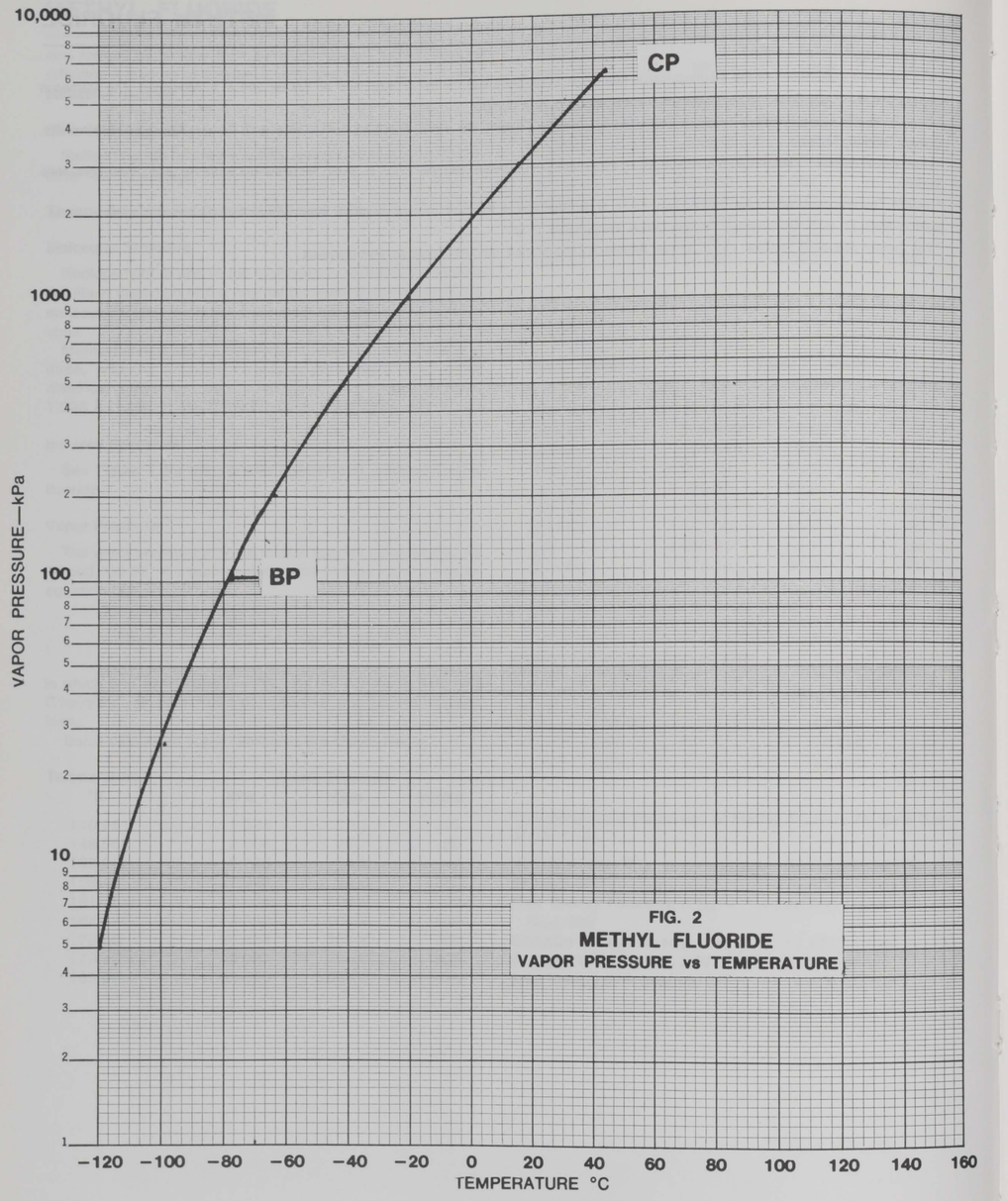


FIG. 2
METHYL FLUORIDE
VAPOR PRESSURE vs TEMPERATURE

Matheson

METHYL MERCAPTAN

(Synonym: Methanethiol)
(Formula: CH_3SH)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.048 103 kg
One Mole of CH_3SH	0.048 103 kg
Specific Volume @ 21.1 °C, 101.325 kPa	499.4 dm^3/kg; 8.0 ft^3/lb
Vapor Pressure @ 21.1 °C	205 kPa; 2.05 bar; 29.7 psia; 2.02 atm
Boiling Point @ 101.325 kPa	279.95 °K; 6.8 °C; 44.2 °F
Melting Point	150.15 °K; −123.0 °C; −189.4 °F
Transition Point	137.59 °K; −135.6 °C; −212.0 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	1.999 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	1.66
Density, Liquid @ Saturation Pressure @ 21.1 °C	0.866 kg/dm^3
Critical Temperature	469.95 °K; 196.8 °C; 386.2 °F
Critical Pressure	7 230 kPa; 72.3 bar; 1 049.3 psia; 71.4 atm
Critical Volume	3.014 dm^3/kg
Critical Density	0.332 kg/dm^3
Critical Compressibility Factor	0.268
Latent Heat of Fusion @ −123.0 °C	122.792 kJ/kg; 29.348 kcal/kg
Heat of Transition @ −135.6 °C	4.56 kJ/kg; 1.09 kcal/kg
Flammability Limits In Air	3.9–21.8% (by volume)
Flash Point (Open Cup)	<255.15 °K; <20 °C; <0 °F
Dipole Moment, Gas	5.07×10^{-30} C·m; 1.52 D
Molar Specific Heat, Gas @ 101.325 kPa @ 15.6 °C	
@ Constant Pressure	49.491 J/(mol·°K)
@ Constant Volume	41.239 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 15.6 °C, Cp/Cv	1.200
Molar Specific Heat, Liquid @ Saturation Pressure @ −21.1 °C	88.415 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.009 4 mPa·s; 0.009 4 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.013 26 W/(m·°K) 31.7×10^{-6} cal·cm/(s·cm^2·°C)
Solubility In Water @ 101.325 kPa @ 15 °C	2.4% (by weight)

Description

At room temperature and atmospheric pressure, methyl mercaptan is a colorless, flammable, toxic gas with an extremely disagreeable odor. It is readily liquefied and is shipped in steel cylinders and ton containers under its own vapor pressure of 103 kPa (15 psig) at 21.1 °C.

Specifications

Methyl mercaptan has a minimum purity of 99.5%.

Uses

CH_3SH has been used in organic synthesis and is an intermediate for jet fuel additives, fungicides, and methionine.

Effects In Man and Toxicity (2)

In high concentrations, methyl mercaptan attacks the central nervous system and causes muscular weakness, tremors, unconsciousness and respiratory paralysis. Chief symptoms are irritation of the mucous membranes, general intoxication, occasionally convulsions, pulmonary irritation and more or less pronounced paralysis of the locomotor muscles and the respiration.

High concentrations of vapor or liquid methyl mercaptan may irritate the eyes and skin.

The extremely disagreeable odor of methyl mercaptan provides adequate warning of its presence, at levels far below those which produce toxicological effects.

Matheson

Threshold Limit Value (TLV)

The 1979 ACGIH has recommended at Threshold Limit Value (TLV) of 0.5 ppm (1 mg/m^3) for methyl mercaptan.

First Aid Treatment (2)

Inhalation

Workers showing symptoms or signs of methyl mercaptan poisoning should be removed immediately to an uncontaminated area (care should be taken by the rescuers that they are adequately protected from inhalation of the toxic vapors). The victim should be kept warm and at complete rest. If breathing is difficult or has stopped, artificial respiration should be started at once, and preferably with simultaneous administration of oxygen. Observe for premonitory signs of pulmonary edema.

Eyes or Skin

In case of skin or eye contact with high concentrations of vapor or liquid methyl mercaptan, wash the skin or irrigate the eyes promptly with water. Severe pain in the eyes from conjunctivitis may be controlled by hot and cold compresses.

Suggested Medical Treatment (2)

The use of respiratory stimulants, such as caffeine and sodium benzoate 7.5 grains (0.000 5 kg), coramine (0.5 cm^3, intramuscularly or preferably intravenously), camphor in oil (1–2 cm^3, intramuscularly), or metrazol (1.5 grains (0.000 1 kg)), may be of value because of the central character of the respiratory failure.

Precautions in Handling and Storage

The hazards associated with the use of CH_3SH are due to its extreme flammability and to its stench properties.

(a) Store and use cylinders containing CH_3SH only in well-ventilated areas (preferably hoods with forced draft ventilation) away from heat and all sources of ignition such as flames or sparks.

(b) Ground all lines and equipment to contain CH_3SH.

(c) Never use flames to detect flammable gas leaks, use soap water solution.

(d) Do not use CH_3SH around sparking motors or other non-explosion-proof equipment.

(e) Do not store reserve stocks of cylinders containing CH_3SH with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials.

(f) Personnel handling CH_3SH should wear chemical safety goggles, rubber gloves, appropriate gas masks, and safety shoes.

(g) An air-line or oxygen mask should be kept available in convenient locations for emergencies.

(h) Eye-washing facilities and safety showers should be available for use in emergencies.

(i) Non-sparking tools are preferred for use with CH_3SH.

(j) If spills occur, immediately apply liquid household bleach, calcium or sodium hypochlorite in aqueous solution. Do not use powdered bleach.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks of CH_3SH in lines and equipment may be detected by applying soap water solution to the suspected sites. Leaks will be evident by bubble formation.

Analytical Detection

Atmospheric concentrations may be determined by drawing the air slowly through a wash bottle containing 1 ml of isatin-sulfuric acid solution (freshly prepared solution of 0.000 10 kg isatin in 100 ml concentrated sulfuric acid). The mercaptan turns the reagent a grass green color. The amount of CH_3SH can be estimated colorimetrically within the range of $5.0 \times 10^{-9} - 10.1 \times 10^{-6}$ kg by the depth of the color developed, the latter being compared with known standards.

Matheson supplies a Toxic Gas Detector Model 8014K for determination of CH_3SH in the range of 5–140 ppm in air with the Model 164S detector tube. A 100-ml sample of the atmosphere is drawn through the detector tube containing a chemical reagent which absorbs and reacts with CH_3SH. The color stain produced varies in length according to the concentration of the CH_3SH being measured. The length of the stain, and hence the concentration, is read directly from the tube.

Disposal of Leaking Cylinders

Several disposal procedures can be used.

(a) The method described in Appendix II-D.

(b) Absorption in a suitable organic solvent (methanol, ethanol, benzene) and subsequent recovery from the solution.

(c) The CH_3SH may be oxidized to CH_3SSCH_3 by introducing it into a 5–10% oxidizing solution such as hydrogen peroxide, sodium hypochlorite, sodium hypobromite, or calcium hypochlorite.

Materials of Construction

Stainless steel and steel alloys (copper free) are preferred materials of construction for handling CH_3SH. In particular, stainless steel should be used with any vessels or lines which are to be opened and exposed to the air frequently. Aluminum is also suitable but caution is advised if it is to be used for CH_3SH under pressure.

Plain iron and steel are less preferred than the above materials. However, they can be used safely if they are first conditioned by exposure to CH_3SH or hydrogen sulfide and subsequently maintained under a dry, inert atmosphere.

Brass, although tarnished by dry CH_3SH, does not seem to be adversely affected.

Vulcabeston gaskets are satisfactory, as is Teflon.

Cylinder and Valve Description

CH_3SH is packaged in DOT approved, low pressure, steel cylinders. Matheson cylinders containing CH_3SH are equipped with the alternate standard Compressed Gas Association (CSA) cylinder valve outlet connection No. 330. The valve outlet has a thread size of 0.825 inch, with left-hand external threads with a flat seat and using a washer as a seal (see Figure 1 for an illustration). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet.

The packing nut at the top of the valve should be kept tight

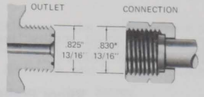


Fig. 1. **CONNECTION 330** .825"-14 LH EXT. used with Flat Seat and Washer

at all times (to tighten it should be turned clockwise as viewed from above). If leaks persist call the supplier immediately.

Only large (285 lb net) cylinders of CH_3SH are equipped with dip tubes for removal of liquid CH_3SH. Other cylinders must be inverted to obtain the liquid.

Safety Devices

Although not required by the DOT the cylinder valve used by Matheson contains fusible metal plug, melting about 73.9 °C (165 °F), as a safety device.

Recommended Controls

Automatic Pressure Regulators

Single stage regulator Model 13-330 is recommended for use with methyl mercaptan. This regulator has an anodized aluminum body, with type 316 stainless steel internal parts, a diaphragm of FEP Teflon on Neoprene, and a Teflon seat. It has a delivery pressure range of 28-240 kPa (4–35 psig). No cylinder pressure gauge is provided since it would not indicate cylinder content but only vapor pressure, which will remain constant as long as any liquid methyl mercaptan is present in the cylinder. A stainless steel check valve is recommended for use with the regulator.

The Matheson Model 71-330 regulator is designed for sensitive and very accurate low pressure control. The regulator has an oversize, pancake, aluminum body, a Teflon-faced Butyl rubber diaphragm, a Teflon seat, and type 303 stainless steel internal parts. It has a delivery pressure range of 3.4–34.5 kPa (0.5–5.0 psig).

Manual Controls

Matheson needle valve Model 61-330, of stainless steel, is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a hose connection, 1/4" tube fitting, or 1/4" NPT male or female pipe. A Model 32S or Model 59 is available for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

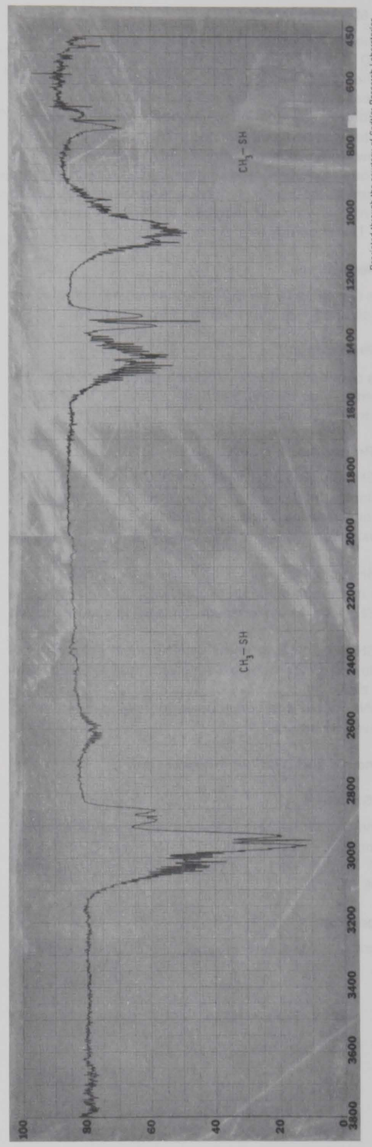


Fig. 2. Infrared spectrum of gaseous methyl mercaptan over the frequency range of 3 800 cm^{-1} to 450 cm^{-1}; 10 cm path length cell, with KBr optics; cell pressure (complete scan): 6.666 kPa (50 mmHg) (6).

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

CH_3SH is classified by the DOT as a flammable, compressed gas and is shipped with the required "Red Gas Label".

Chemical Preparation

CH_3SH is obtained by the reaction of aqueous sodium hydrosulfide, methyl chloride, and hydrogen sulfide, or from methanol and hydrogen sulfide.

Chemical Properties

(a) CH_3SH, on oxidation with concentrated sulfuric acid, sulfuryl chloride, hydrogen peroxide, sodium hypohalite, or iodine, is converted into dimethyl disulfide.

(b) On oxidation with nitric acid, CH_3SH forms methanesulfonic acid.

(c) CH_3SH combines with aldehydes and ketones giving mercaptals and mercaptols, respectively.

(d) CH_3SH adds to an ethylene linkage to give a dialkyl sulfide.

(e) CH_3SH is acidic and forms water-soluble salts with the alkali metals and water-insoluble salts with heavy metals (mercury, lead, zinc).

(f) CH_3SNa reacts with compounds containing reactive halogens to give thio ethers.

Thermodynamic and Detailed Physical Data

Molecular Structure

Methyl mercaptan has the following structural parameters: bond distances: C—H 1.10 Å (1.10×10^{-10} m); C—S 1.82 Å (1.82×10^{-10} m); S—H 1.33 Å (1.33×10^{-10} m); bond angle: C—S—H 96.5°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous methyl mercaptan.

Vapor Pressure

The vapor pressure of liquid methyl mercaptan below 101.325 kPa (1 atm) is shown below (3).

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
182.45	0.133	1.33	1
197.85	0.667	6.67	5
205.65	1.333	13.3	10
214.35	2.666	26.7	20
223.95	5.333	53.3	40
230.05	7.999	80.0	60
238.35	13.332	133.3	100
251.05	26.664	266.6	200
265.25	53.329	533.3	400
279.95	101.325	1 013.25	760

The vapor pressure of liquid methyl mercaptan above 101.325 kPa (1 atm) is listed below (4).

Temperature, °K	Vapor Pressure kPa	bar	atm
279.95	101.325	1.013 25	1
299.25	202.650	2.03	2
329.05	506.625	5.07	5
356.55	1 013.25	10.13	10
390.65	2 026.50	20.27	20
413.15	3 039.75	30.40	30
430.85	4 053.00	40.53	40
445.15	5 066.25	50.66	50
458.15	6 079.50	60.80	60

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/kg
253.15	537.4
273.15	511.6
279.15	510.9

Thermodynamic Properties of Methyl Mercaptan As Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	50.250 J/(mol·°K)
Entropy, S°	255.015 J/(mol·°K)
Gibbs Energy Function, $(G_{298}^\circ - H_0^\circ)/298$	−214.346 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	12.125 kJ/mol
Enthalpy of Formation, ΔH_f°	−86.525 kJ/mol
Gibbs Energy of Formation, ΔG_f°	−49.036 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of methyl mercaptan, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, 1975, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, 1977, pp. 100–103, Matheson, Lyndhurst, New Jersey.

[3] *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, 1973, p. 3-56, McGraw-Hill Book Co., Inc., New York, New York.

[4] **Ibid.**, p. 3-62.

[5] M. Z. El-Sabban and D. W. Scott, *The Chemical Thermodynamic Properties of Hydrocarbons and Related Substances II. Properties of 25 Organic Sulfur Compounds in the Ideal Gas State from 0 to 1 000 °K*, 1970, pp. 1–26, Bur. of Mines Bull. 654, U. S. Government Printing Office, Washington, D. C.

[6] *The Sadtler Standard Spectra*, 1972, Sadtler Research laboratories, Inc., Philadelphia, Pennsylvania.

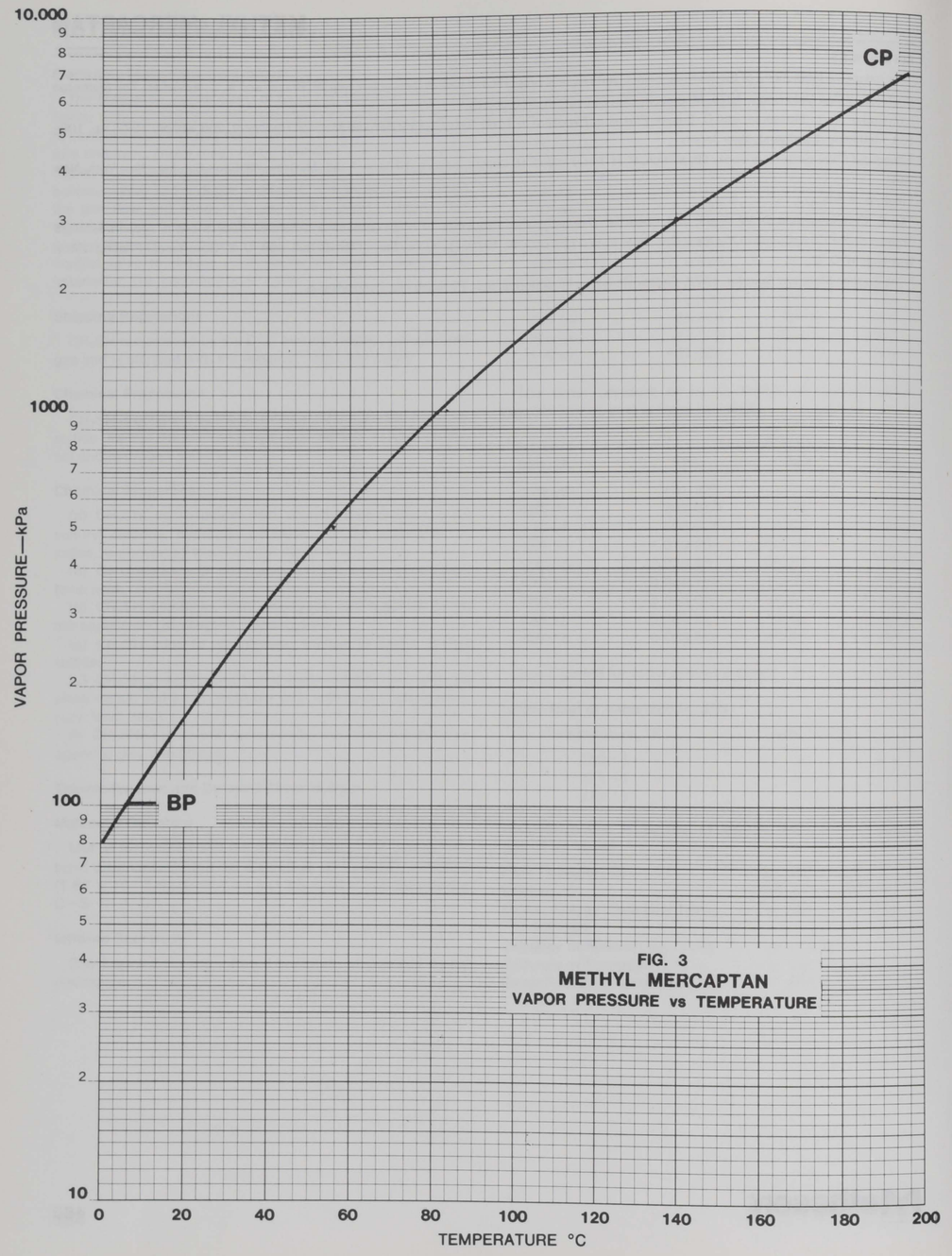


FIG. 3
METHYL MERCAPTAN
VAPOR PRESSURE vs TEMPERATURE

METHYL VINYL ETHER

(Synonyms: Vinyl Methyl Ether; Methoxyethylene)
(Formula: $CH_3OCH{:}CH_2$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.058 080 kg
One Mole of $CH_3OCH{:}CH_2$	0.058 080 kg
Specific Volume @ 21.1 °C, 101.325 kPa	418.3 dm^3/kg; 6.7 ft^3/lb
Vapor Pressure @ 20 °C	174 kPa; 1.74 bar; 25.3 psia; 1.72 atm
Boiling Point @ 101.325 kPa	278.65 °K; 5.5 °C; 41.9 °F
Freezing Point In Air @ 101.325 kPa	151.15 °K; −122.0 °C; −187.6 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	2.395 8 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	1.99
Density, Liquid @ Saturation Pressure @ 0 °C	0.776 8 kg/l
Critical Temperature	436.70 °K; 163.6 °C; 326.4 °F
Critical Pressure	4.666 kPa; 46.66 bar; 676.8 psia; 46.05 atm
Critical Volume	3.530 dm^3/kg
Critical Density	0.283 kg/dm^3
Critical Compressibility Factor	0.263
Flammability Limits In Air	~1.9 −30.0% (by volume)
Flash Point (open cup)	217.04 °K; −56.1 °C; −69.0 °F
Dipole Moment, Gas	3.24×10^{-30} C.m; 0.97 D
Solubility In Water @ 101.325 kPa @ 25 °C	0.82% (by weight)
Refractive Index, Liquid @ Saturation Pressure, n_D @ 25 °C	1.3947

Description

At room temperature and atmospheric pressure, methyl vinyl ether is a colorless, highly flammable gas having a sweet, pleasant odor. It is easily liquefied and is shipped in steel cylinders as a liquefied gas under its own vapor pressure of 73 kPa (10.6 psig) at 20 °C.

Specifications

Methyl vinyl ether has a minimum purity of 99.5%.

Uses

Methyl vinyl ether has been used to prepare homopolymers and copolymers; as a plasticizer for nitrocellulose and other plastics; as an intermediate in organic synthesis.

Effects In Man and Toxicity (2)

Like ethyl ether, the principal physiological effect of methyl vinyl ether is that of anesthesia, but the anesthetic effect is much less (about ¼) than that produced by ethyl ether. Concentrations of 5–20% by volume cause such symptoms as intoxication, incoordination, blurring of vision, anesthesia, headache, dizziness, excitation, sick feeling and unconsciousness, depending on the duration of exposure.

Exposure of the eyes or mucous membranes to the liquid or concentrated vapor is irritating and should be avoided.

Contact of the liquid or concentrated vapor with the skin can cause frostbite.

Methyl vinyl ether has a low order of inhalation toxicity. It is not known to possess adequate warning properties. Concentrations which produce any of the above mentioned symptoms should be considered excessive.

No Threshold Limit Value (TLV) has been recommended by the 1979 ACGIH for methyl vinyl ether.

First Aid (2)

Inhalation

If the victim feels dizzy, sick or has a headache or blurred vision, he should go to an uncontaminated area and inhale fresh air.

Eyes

In case of contact with the eyes, wash them with copious quantities of water for at least 15 minutes. A physician, preferably an eye specialist, should be called at once.

Skin

In case frostbite develops as a result of contact of methyl vinyl ether with the skin, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten,

have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

The hazards in handling methyl vinyl ether stem from its extreme flammability. All equipment used with methyl vinyl ether should be grounded. Store and use methyl vinyl ether in well-ventilated areas away from heat and all sources of ignition such as flames and sparks. Never use flames to detect leaks, use soap water solution. Do not use methyl vinyl ether around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of cylinders of methyl vinyl ether with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks in lines and equipment containing methyl vinyl ether may be detected by painting the suspected points with soap water solution; leaks will be indicated by bubble formation.

Disposal of Leaking Cylinders

Leaking cylinders of methyl vinyl ether which cannot be corrected normally may be handled in the following manner. Remove cylinder to a hood with forced ventilation. Attach appropriate regulator and check valve to the cylinder valve outlet. Introduce the gas into a dry, neutral, suitable solvent such as benzene, toluene, xylene, or acetone. Recover the product from the resulting solution by distillation, taking all precautions to prevent ingress of moisture and acid vapors.

Materials of Construction

Since methyl vinyl ether is noncorrosive, the common structural metals may be used, except copper and its alloys which could form explosive acetylides with the acetylene present in methyl vinyl ether as an impurity.

Cylinder and Valve Description

Methyl vinyl ether is shipped in DOT approved, low pressure steel cylinders. These cylinders are equipped with steel or cadmium-plated brass valves having Compressed Gas Association (CGA) alternate valve outlet connection No. 290. The valve outlet has a thread size of 0.745 inch, with left-hand external threads accepting a bullet-shaped nipple (see Figure 1 for an illustration). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet.

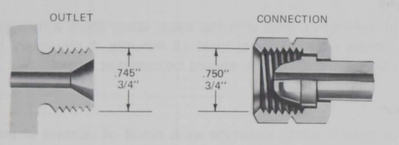


Fig. 1. CONNECTION 290 .745″-14 LH EXT. accepting a Bullet Shaped Nipple

Safety Devices

The most commonly used safety device, and the one used by Matheson, is the spring-loaded safety relief valve. If the cylinder pressure becomes dangerously high, usually due to overheating, the safety relief device will open (at about 2 590 kPa (375 psig)) and release gaseous methyl vinyl ether until the pressure again returns to a safe level.

Recommended Controls

Automatic Pressure Regulators

Sensitive and very accurate low pressure regulation can be obtained with regulator Model 71-290. This regulator has an oversize, pancake body of aluminum, a Teflon-faced Butyl rubber diaphragm, a Teflon seat, and type 303 stainless steel internal parts. It has a delivery pressure range 3.4–34.5 kPa (0.5–5.0 psig).

Manual Controls

Matheson needle valve Model 61-290 of type 303 stainless steel is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a hose connection, ¼″ tube fitting or ¼″ NPT male or female pipe. It should be used only where manual flow control is needed and should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. Stainless steel needle valve Model 32S or Model 59 is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Matheson

Shipping Regulations

Methyl vinyl ether is classified by the DOT as a flammable compressed gas and is shipped with the required "Red Gas Label."

Commercial Preparations

Methyl vinyl ether is obtained by a vinylation reaction: by treating acetylene with methanol in the presence of potassium hydroxide. It is also prepared by converting acetaldehyde (with methanol) into dimethyl acetal (1,1-dimethoxyethane), and subjecting the acetal to pyrolysis.

Chemical Properties

Since methyl vinyl ether is a reactive chemical and is sensitive to acidic materials, every precaution must be taken to avoid accidental contact with acids or acidic substances. Methyl vinyl ether undergoes the following reactions[1]:

(a) Hydrolysis, which occurs rapidly with dilute aqueous acids or slowly by hot water, to give acetaldehyde and methanol.

(b) Hydrogenation, in the presence of catalysts, to methyl ethyl ether.

(c) Acetalization, by addition of alcohols in the presence of an acid catalysts, to give both symmetrical and mixed acetals.

(d) Addition, with chlorine, bromine, hydrogen chloride, and hydrogen bromide, to give α,β-dichloro- or dibromoethyl methyl ether and α-chloro- or α-bromoethyl methyl ether, respectively. These additions are extremely vigorous and may be explosive so that controlled conditions must be used, such as inert solvents and low temperatures.

(e) Addition, with organic acids, to give α-methoxyethylidene esters.

(f) Addition, with hydrogen cyanide, in the presence of pyridine under pressure at 100–150 °C, to form α-cyanoethyl methyl ether.

(g) Cyclization, with ammonia, at 200 °C and 200 atmospheres pressure in the presence of a cuprous chloride-ammonium chloride catalyst, to form 2-methyl-5-ethylpyridine.

(h) Polymerization and copolymerization, with various unsaturated compounds.

(i) Diels-Alder condensation with conjugated unsaturated aldehydes or ketones, e.g., with acrolein, 2-methoxydihydropyran is readily formed.

(j) Reacts with a secondary amine, such as morpholine, piperidine, or pyrrolidine, and sulfur to give N-substituted thioacetamides.

(k) Reacts with hydroxythiols (e.g., $HSCH_2CH_2OH$) in the presence of an amine catalyst to form monoethers of thiodiglycols (e.g., $CH_3OCH_2CH_2SCH_2CH_2OH$).

Thermodynamic and Detailed Physical Data

Molecular Structure

Methyl vinyl ether is a planar molecule having the following approximate structural parameters: bond distances: C═C 1.344 Å (1.344 × 10^{-10} m); H_2C:HC—O 1.325 Å (1.325 × 10^{-10} m); O—CH 1.453 Å (1.453 × 10^{-10} m); bond angles: C═C—O 125°; C—O—C 120°.

Infrared Spectrum

For the infrared spectrum of gaseous methyl vinyl ether, see Figure 2.

Vapor Pressure (3)

The vapor pressure of liquid methyl vinyl ether above 101.325 kPa (1 atm) is shown below:

Temperature, °K	Vapor Pressure kPa	bar	atm
278.65	101.325	1.01325	1.00
293.15	174.437	1.74	1.72
303.15	244.764	2.45	2.42
313.15	337.843	3.38	3.33
323.15	455.054	4.55	4.49
333.15	599.844	6.00	5.92
343.15	772.213	7.72	7.62
353.15	979.055	9.79	9.66
363.15	1 220.372	12.20	12.0
373.15	1 516.846	15.17	15.0
383.15	1 827.111	18.27	18.0
393.15	2 192.533	21.93	21.6
403.15	2 599.323	25.99	25.7
413.15	3 040.588	30.41	30.0
423.15	3 543.905	35.44	35.0
433.15	4 067.906	40.68	40.2

Latent Heat of Vaporization, ΔHv @ 5.5 °C	24.518 kJ/mol; 5 860 cal/mol
Heat Capacity, Ideal Gas, C_p^o @ 25 °C	77.03 J/(mol·°K)

REFERENCES

1. For extensive tabulations of the thermodynamic and physical properties of methyl vinyl ether, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.
2. W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, 1977, pp. 7–11, Matheson, Lyndhurst, New Jersey.
3. *Methyl Vinyl Ether*, Tech. Bull. 7543-086, General Aniline & Film Corporation, New York, New York.
4. *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Matheson

©Sadtler 1972

Reprinted through the courtesy of Sadtler Research Laboratories

Fig. 2. Infrared spectrum of gaseous methyl vinyl ether over the frequency range of 3 800 to 450 cm^{-1}; 10 cm path length cell, with KBr optics; cell pressure: curve A (complete scan): 6.666 kPa (50 mmHg) curve B (partial scan): 0.667 kPa (5 mmHg) (4).

Matheson®

FIG. 3
METHYL VINYL ETHER
VAPOR PRESSURE vs TEMPERATURE

MONOETHYLAMINE

(Synonyms: Ethylamine; Aminoethane)
(Formula: $C_2H_5NH_2$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.045 085 kg
One Mole of $C_2H_5NH_2$	0.045 085 kg
Specific Volume @ 21.1 °C, 101.325 kPa	536.9 dm^3/kg; 8.6 ft^3/lb
Vapor Pressure @ 20 °C	117 kPa; 1.17 bar; 16.9 psia; 1.15 atm
Boiling Point @ 101.325 kPa	289.73 °K; 16.6 °C; 61.8 °F
Freezing Point In Air @ 101.325 kPa	192.15 °K; −81.0 °C; −113.8 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	1.912 kg/dm^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.61
Density, Liquid @ Saturation Pressure @ 25 °C	0.676 9 kg/l
Critical Temperature	456.15 °K; 183.0 °C; 361.4 °F
Critical Pressure	5620 kPa; 56.2 bar; 815.6 psia; 55.5 atm
Critical Volume	4.103 dm^3/kg
Critical Density	0.244 kg/dm^3
Critical Compressibility Factor	0.274
Flammability Limits In Air	3.5–14.0% (by volume)
Dipole Moment, Gas	4.0×10^{-30} C·m; 1.2 D
Molar Specific Heat, Liquid	129.7 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.008 0 mPa·s; 0.008 0 cP
Viscosity, Liquid @ 10 °C	0.282 mPa·s; 0.282 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.014 59 W/(m·°K); 34.9×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 15 °C	20.56 mN/m; 20.56 dyn/cm
Autoignition Temperature	657 °K; 384 °C; 723 °F
Flash Point (open cup)	255.15 K; −20 °C; 0 °F
Refractive Index, Liquid @ Saturation Pressure @ 25 °C	1.362 7
Dielectric Constant, Liquid @ 10 °C	6.94
Heat of Combustion, Liquid @ 20 °C and 101.325 kPa Gross, to form H_2O (liq) + CO_2 (gas) + N (gas)	1 709.2 kJ/mol

Description

Monoethylamine is a water-white, flammable, low-boiling liquid having a strong ammoniacal odor. It is shipped as a liquid under its own vapor pressure of 15 kPa (2.2 psig) at 20 °C.

Specifications

Monoethylamine as supplied by Matheson has a purity of 98.5% (liquid phase).

Uses

Monoethylamine is used principally as an intermediate in the manufacture of dyes, drugs, emulsifying agents and other synthetic organic compounds, and as a solvent.

Effects In Man and Toxicity (2)

Exposure to vapors of monoethylamine produces eye irritation with lacrimation, conjunctivitis and corneal edema. Inhalation of higher concentrations (more than 100 ppm) of monoethylamine causes irritation of the mucous membranes of the nose and throat and lung irritation with respiratory distress and cough. The vapors may also produce primary skin irritation and dermatitis. Direct local contact with liquid monoethylamine produces severe and sometimes permanent eye damage or skin burns.

No definite human toxicity data are available, although the above described physiological effects from relatively low concentrations of vapor have been recorded.

Though monoethylamine is readily detectable in air by odor, the olfactory sense may become fatigued on continuous inhalation. Odor then is no longer a reliable warning property of the presence of dangerous concentrations of these vapors.

The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 10 ppm (18 mg/m^3) for monoethylamine.

First Aid Treatment (2)

The following suggested first aid treatments should be administered promptly.

Inhalation

Workers overcome by monoethylamine should be removed to fresh air at once and given oxygen until the arrival of the physician. If breathing has stopped, artificial respiration and oxygen should be administered simultaneously. The patient should be kept warm and quiet. No alcoholic stimulants should be administered. Oxygen and antispasmodic drugs may help to relieve coughing.

Nose and Throat

Irrigate nose and mouth continuously for 15 minutes. If the patient can swallow, encourage him to drink large quantities of ½% citric acid solution or lemonade.

Skin Contact

Remove contaminated clothing and immediately flush the affected area of the body with large quantities of water. Since the reaction is alkaline, the skin should be washed with a mild acidic solution such as vinegar of 1–2% acetic solution.

Use no ointments on the skin during the first 24 hour period after the injury. Do not cover the injured area with clothing or a dry dressing. During the first 24 hours, the area may be covered with a dressing and kept moist with a physiological salt solution (0.9% sodium chloride). Dermatitis may be produced from contact with the skin.

Eye Contact

1. Immediately flush thoroughly with water, holding the lids wide open. Continue irrigation for at least 15 minutes.
2. After the irrigation is completed, instill 2 or 3 drops of a 0.5% pontocaine solution. This relieves the pain.
3. After the pain disappears (this may require a few minutes), flush the eyes with water or preferably physiological salt solution (0.9% sodium chloride).
4. Put 1 drop of fluorescein (eye-stain) into each eye and wash the eyes for 2 minutes with water. If the eye has been injured, a green stain will appear over the injured area.
5. If the eyeball stains green anywhere, put 1 more drop of pontocaine in the eye, wash the eye for 15 minutes (as shown under item 3) and restain with a drop of fluorescein.
6. Wash the eye for 2 minutes (item 3). If the eyeball stains green, take the patient to an eye specialist immediately, but do not stop the first aid treatment to take the patient to an eye specialist until items 1 through 6 have been completed.

Do not apply eye pads or pressure, as gluing of the lids to the eyeball will occur.

Precautions in Handling and Storage

The hazards in handling monoethylamine are due to its toxicity and extreme flammability. Store and use monoethylamine in well-ventilated areas away from heat and all ignition sources such as flames and sparks. Never use flames to detect monoethylamine leaks. Do not use monoethylamine around sparking motors and other non-explosion-proof equipment. Do not store stocks of monoethylamine cylinders and cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all lines and equipment used with monoethylamine.

Aside from the above general precautions, the following rules should be observed:

1. Anyone working with monoethylamine should wear rubber gloves, chemical goggles, and a rubber or plastic apron.
2. Monoethylamine cylinders should never be directly heated by steam or flames. Uncontrolled heating of a cylinder can cause the liquid to expand to a point where dangerous hydrostatic pressures will be developed. Any heating should be done in a thermostated water or oil bath. The temperature should not be allowed to exceed 51.7 °C (125 °F). Cylinders of monoethylamine are not equipped with safety devices.
3. Withdrawal of monoethylamine should be performed in a well-ventilated area or in a hood.
4. A gas mask approved by NIOSH, showers and an eye bath should be conveniently located in case of emergency.
5. Weigh monoethylamine cylinders to determine the net contents. The Matheson Model 8510 Cylinder Scale is ideal for this purpose. The tare weight is stamped on all cylinders.
6. Manifolded cylinders of monoethylamine should have check valves at the cylinder outlets to prevent the exchange of material from one cylinder to another causing a cylinder to become overfull.
7. Flames and sparks should not be allowed in an area where monoethylamine is being used.
8. A trap or check valve should be used to prevent suckback of foreign materials into a cylinder of monoethylamine. Suckback can cause an extremely corrosive condition to form, aside from the possibility of having a violent reaction take place within the cylinder. Any accidental suckback should be immediately reported to the supplier.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Never use flames to detect monoethylamine leaks. Leaks can be detected by passing an open bottle or a squeeze bottle containing hydrochloric acid in the vicinity of the suspected leak. Dense white fumes will be formed in the area of the leak. Wet red litmus or phenolphthalein paper will undergo a color change with monoethylamine and are of aid in detecting small leaks.

Leaks which cannot be stopped should be covered with wet rags in order to prevent the atmosphere from becoming contaminated with monoethylamine.

Cylinder valves may develop leaks through the packing which can be stopped by tightening up the packing nut, by turning it

counter clockwise. Leaks through the valve outlet that cannot be stopped should be stopped by plugging the outlet with 3/8" pipe plugs.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-B.

Materials of Construction

Iron and steel are recommended for all equipment coming in contact with monoethylamine. Copper, tin, zinc and their alloys are attacked by moist monoethylamine and should not be used. Piping should be rigid steel except where short connections are required such as between cylinders and manifold or pipe lines. For these applications, a steel reinforced neoprene line is recommended.

For permanent installations, tongue and groove, flanged fittings with lead or asbestos composition gaskets are recommended. In order to reduce maintenance on leaks all joints should be welded wherever possible.

Cylinder and Valve Description

Cylinder valves are made of forged steel and are of the packed type. The valve outlet designated as the alternate standard for monoethylamine by the Compressed Gas Association (CGA) is connection No. 240. The thread specifications are 3/8"-18NGT-INT accepting a tapered threaded pipe (see Figure 1 for the drawing and specifications on this valve outlet and its mating connection). Lecture bottles have a special 5/16"-32 threads per inch, female valve outlet.

Cylinders containing 15 lb or more of monoethylamine are usually equipped with goose neck dip-tubes. Withdrawal of vapor is accomplished by placing the cylinder in its normal vertical position. On occasion, a full cylinder standing in the sun will heat up and cause the liquid to expand and cover the end of the dip-tube. In this case, it is necessary to allow the cylinder to cool before the vapor can be withdrawn or the cylinder should be placed in a horizontal position with the valve outlet facing down.

To withdraw liquid the cylinder should be placed in a horizontal position with the valve outlet facing up.

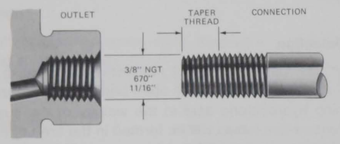


Fig. 1. CONNECTION 240 3/8"-NGT RH INT. IPS accepting Tapered Threaded Pipe

Safety Devices

Since no safety devices are used in monoethylamine cylinders, extra precautions should be used to prevent cylinders from being exposed to heat, which could cause an uncontrolled hydrostatic pressure build-up.

Recommended Controls

Manual Controls

Manual needle valve Model 61-240 of type 303 stainless steel is available for direct attachment to the cylinder valve outlet. Stainless steel needle valve Model 32S or Model 59 is recommended for use with lecture bottles.

Shipping Regulations

Monoethylamine is shipped as a flammable liquid, taking a DOT "Red Label".

Commercial Preparations

Monoethylamine is produced industrially by the interaction of ammonia and ethyl bromide and subsequently treating the reaction product with alkali. The crude base is then fractionated to remove the simultaneously formed di- and triethylamines.

Chemical Properties

Monoethylamine reacts with esters, acid chlorides, or acid anhydrides forming N-ethyl amides; formyl derivatives are obtained by reaction with formic acid; with diethyl oxalate, N,N'-diethyloxamide is formed. Monoethylamine upon treatment with benzenesulfonyl chloride and aqueous alkali gives N-ethylbenzenesulfonamide, which is soluble in excess aqueous alkali. Nitrous acid reacts with monoethylamine forming ethyl alcohol, nitrogen, and water. With formaldehyde in the presence of alkali, monoethylamine forms either N-hydroxymethylethylamine or bis(ethylamino)methane. In the presence of acids, formaldehyde methylates monoethylamine. Other aliphatic and aromatic aldehydes react with monoethylamine forming Schiff bases. The phenolic hydroxyl group in naphthols may be replaced by heating the naphthols with monoethylamine sulfite. Monoethylamine reacts with carbon disulfide giving a monoethylamine salt of ethyldithiocarbamic acid. Monoethylamine is relatively stable to acid permanganate, but is readily attacked in alkaline solution giving ammonia and acetaldehyde or acetic acid. Lead dioxide acts similarly. Persulfuric acid, hydrogen peroxide, peracetic acid, and perbenzonic acid effect addition of oxygen to monoethylamine forming first N-ethylhydroxylamine which is further oxidized to acetohydroxamic acid.

The unsubstituted amino hydrogens are replaceable by the action of chlorine, bromine and iodine, either alone or in the presence of alkali. Monoethylamine on warming with chloroform and alkali forms ethyl isocyanide (carbylamine reaction). Monoethylamine reacts with substituted or unsubstituted isocyanic and isothiocyanic acids forming substituted ureas and thioureas. Monoethylamine reacts with methylmagnesium iodide forming ethylaminomagnesium iodide and methane. Aromatic and heterocylic compounds containing reactive halogen atoms react with monoethylamine, e.g., 2,4,6-trinitrochlorobenzene with monoethylamine give N-ethyl-2,4,6-trinitroaniline. Monoethylamine reacts with nonmetallic oxy- and sulfochlorides, as well as the chlorides of inorganic acids, the ethylamino group replacing one or all of the chlorine atoms.

Matheson

Thermodynamic and Detailed Physical Data

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous monoethylamine.

Vapor Pressure

The vapor pressure of liquid monoethylamine is represented by the following Antoine vapor pressure equation (3):

$$\log_{10} p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 7.386 2, 1 137.30, and 235.85, respectively.

Some calculated vapor pressures are shown below:

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
215.35	1.333	13.33	10
224.15	2.666	26.66	20
233.95	5.333	53.33	40
240.10	7.999	79.99	60
244.72	10.666	106.66	80
248.46	13.332	133.32	100
260.95	26.664	266.64	200
268.98	39.997	399.97	300
275.03	53.329	533.29	400
279.94	66.661	666.61	500
284.11	79.993	799.93	600
287.75	93.325	933.25	700
289.73	101.325	1 013.25	760
290.99	106.658	1 067	800
293.91	119.990	1 200	900
296.59	133.322	1 333	1 000
301.35	159.986	1 600	1 200
307.45	199.983	2 000	1 500

Vapor pressure data above 101.325 kPa (1 atm) are shown below (4).

Temperature, °K	Vapor Pressure kPa	bar	atm
289.75	101.325	1.01325	1
308.85	202.650	2.03	2
338.45	506.625	5.07	5
364.95	1 013.25	10.13	10
397.15	2 026.50	20.27	20
419.15	3 039.75	30.40	30
436.15	4 053.00	40.53	40
449.15	5 066.25	50.66	50
456.35	5 623.54	56.24	55.5

Latent Heat of Vaporization, ΔHv 25 °C . . . . . 610.738 kJ/ g; 145.97 kcal/kg

For ΔHv values at other temperatures, see Table 1.

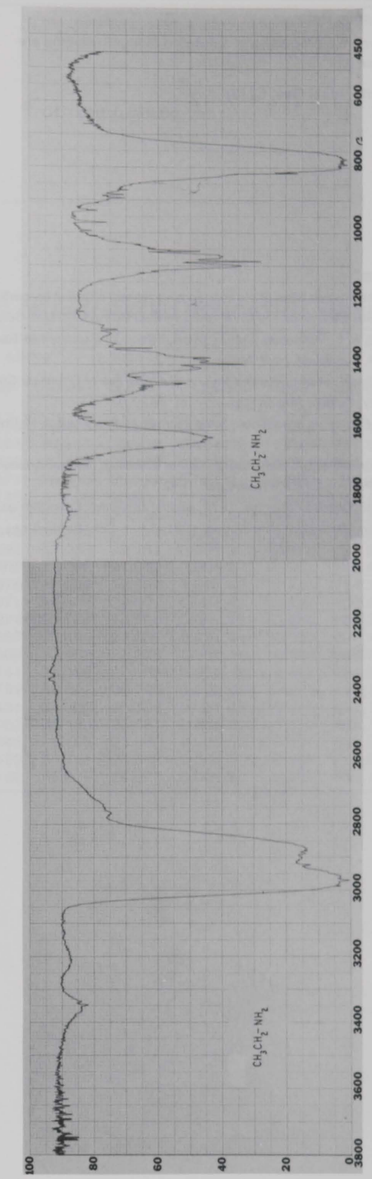


Fig. 2. Infrared spectrum of gaseous monoethylamine over the frequency range of 3 800 cm^{-1} to 450 cm^{-1}; 10 cm path length cell, with KBr optics; cell pressure (complete scan): 3.333 kPa (25 mmHg) (6).

Matheson

Thermodynamic Data

Thermodynamic properties of saturated monoethylamine are listed in Table 1.

Heat Capacity, Ideal Gas, C_p° (5) @ 25 °C	69.873 J/(mol·°K)
Heat Capacity, Liquid, Cs (5) @ 25 °C	129.7 J/(mol·°K)
Enthalpy of Formation, Ideal Gas, ΔH_f° (5) @ 25 °C	−47.154 kJ/mol
Enthalpy of Formation, Liquid (5) @ 25 °C	−74.06 kJ/mol

REFERENCES

1. For extensive tabulations of the thermodynamic and physical properties of monoethylamine, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.
2. W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 51-55, Matheson, Lyndhurst, New Jersey.
3. B. J. Zwolinski, **et al.**, *Selected Values of Properties of Chemical Compounds, 1968*, Volume 1, Thermodynamics Research Center, Texas A & M University, College Station, Texas.
4. *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p. 3-62, McGraw-Hill Book Co., Inc., New York, New York.
5. D. D. Wagman, *et al.*, *Selected Values of Chemical Thermodynamic Properties, 1968*, p. 155, Natl. Bur. Stand. Tech. Note 270-3, U. S. Government Printing Office, Washington, D. C.
6. *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.
7. *Refrigerating Data Book*, 5th edition, *1942*, Amer. Soc. Refrig. Engs., New York, New York.

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED MONOETHYLAMINE (7)

Temperature		kPa Pressure		Entropy J/(mol·°K)		Enthalpy kJ/mol		Latent Heat of Vaporization kJ/mol	Specific Volume m^3/kg		Density kg/m^3	
°K	°F	kN/m^2	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
223.15	−58	2.310	0.023	−4.961	133.818	−0.819	29.826	30.645	0.001 31	16.906	763.4	0.059 2
228.15	−49	3.530	0.035	−2.452	132.234	−0.465	30.147	30.612	0.001 32	12.230	757.6	0.081 8
233.15	−40	5.102	0.050	0.000	130.743	0.000	30.470	30.470	0.001 33	8.397	751.9	0.119 1
238.15	−31	7.260	0.072	2.415	129.347	0.571	30.810	30.239	0.001 34	5.999	746.3	0.166 7
243.15	−22	9.708	0.096	4.772	128.046	1.145	31.089	29.944	0.001 35	4.549	740.7	0.219 8
248.15	−13	13.141	0.130	7.093	126.839	1.723	31.462	29.739	0.001 36	3.427	735.3	0.291 8
253.15	−4	17.554	0.173	9.394	125.707	2.410	31.824	29.414	0.001 37	2.604	729.9	0.384 0
258.15	+5	23.042	0.227	11.677	124.669	2.892	32.053	29.161	0.001 38	2.018	724.6	0.495 5
263.15	14	30.296	0.299	13.921	123.707	3.482	32.362	28.880	0.001 39	1.561	719.4	0.640 6
268.15	23	38.542	0.380	16.166	122.840	4.075	32.669	28.594	0.001 40	1.249	714.3	0.800 6
273.15	32	49.036	0.484	18.449	122.047	4.671	32.973	28.302	0.001 42	0.996	704.2	1.004
278.15	41	61.777	0.610	20.580	121.293	5.274	33.274	28.000	0.001 43	0.084	699.3	1.244
283.15	50	76.980	0.760	22.768	120.614	5.887	33.494	27.607	0.001 44	0.656	694.4	1.524
288.15	59	95.120	0.939	24.938	119.991	6.509	33.882	27.373	0.001 45	0.539	689.7	1.855
293.15	68	116.494	1.150	27.107	119.444	7.141	34.196	27.055	0.001 46	0.447	684.9	2.237
298.15	77	141.480	1.396	29.257	118.935	7.782	34.507	26.725	0.001 48	0.373	675.7	2.681
303.15	86	170.438	1.682	31.389	118.482	8.431	34.820	26.389	0.001 49	0.315	671.1	3.175
308.15	95	204.085	2.014	33.521	118.086	9.052	35.133	26.081	0.001 50	0.267	666.7	3.745
313.15	104	242.420	2.392	35.633	117.728	9.845	35.405	25.560	0.001 52	0.228	657.9	4.386
318.15	113	286.063	2.823	37.708	117.388	10.423	35.761	25.338	0.001 53	0.196	653.6	5.102
323.15	122	335.568	3.312	39.783	117.067	11.102	36.075	24.973	0.001 54	0.169	649.4	5.917

MONOMETHYLAMINE

(Synonyms: Methylamine; Aminomethane)
(Formula: CH_3NH_2)

PHYSICAL PROPERTIES (1)

Molar Mass	0.031 058 kg
Molecular Weight	0.031 058 kg
One Mole of CH_3NH_2	755.4 dm^3/kg; 12.1 ft^3/lb
Specific Volume @ 21.1 °C, 101.325 kPa	300 kPa; 3.0 bar; 43.5 psia; 2.96 atm
Vapor Pressure @ 20 °C	266.82 °K; −6.3 °C; 20.6 °F
Boiling Point @ 101.325 kPa	179.69 °K; −93.5 °C; −136.2 °F
Freezing Point In Air @ 101.325 kPa	1.302 kg/m^3
Absolute Density, Gas @ 101.325 kPa @ 20 °C	1.08
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	0.662 4 kg/l
Density, Liquid @ Saturation Pressure @ 20 °C	430.05 °K; 156.9 °C; 314.4 °F
Critical Temperature	7 460 kPa; 74.6 bar; 1 081.6 psia; 73.6 atm
Critical Pressure	3.960 dm^3/kg
Critical Volume	0.253 kg/dm^3
Critical Density	0.257
Critical Compressibility Factor	197.472 kJ/kg; 47.197 kcal/kg
Latent Heat of Fusion @ −93.5 °C	4.9–20.7% (by volume)
Flammability Limits In Air	4.1 × 10^{-30} C.m; 1.23 D
Dipole Moment, Gas	
Molar Specific Heat, Gas @ 101.325 kPa @ 20 °C	
@ Constant Pressure	51.46 J/(mol·°K)
@ Constant Volume	42.812 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 20 °C, Cp/Cv	1.202
Molar Specific Heat, Liquid @ Saturation Pressure @ −13.9 °C	101.813 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.006 66 mPa·s; 0.006 66 cP
Viscosity, Liquid @ −20 °C	0.321 mPa·s; 0.321 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.015 9 W/(m·°K); 38.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 25 °C	19.19 mN/m; 19.19 dyn/cm
Solubility In Water @ 101.325 kPa @ 25 °C	108 kg/100 kg water
Autoignition Temperature	703.15 °K; 430 °C; 806 °F
Flash Point (open cup)	263.15 °K; −10 °C; 14 °F
Dielectric Constant, Gas @ 100°C	1.003 8
Refractive Index, Liquid @ Saturation Pressure, n_D @ 25 °C	1.349 1
Heat of Combustion, Liquid @ 20 °C and 101.325 kPa Gross, to form H_2O(liq) + CO_2(gas) + N_2(gas)	1 071.52 kJ/mol
Dissociation Constant in Water @ 25 °C kPa	10.62

Description

Monomethylamine is a colorless, flammable gas at room temperature and atmospheric pressure. It has a characteristic fishy odor in lower concentrations, but more like that of ammonia in higher concentrations (100–500 ppm). It is readily liquefied and is shipped as a liquefied gas under its own vapor pressure of 200 kPa (29 psig) at 20 °C.

Uses

Monomethylamine is used in tanning, in the manufacture of dyestuffs, in treatment of cellulose acetate rayon, and in organic synthesis.

Effects In Man and Toxicity (2)

The physiological effects and the toxicological properties of monomethylamine are similar to those described in the preceding data sheet on monoethylamine.

Matheson

First Aid Treatment (2)

The first aid treatments to be followed on exposure to monomethylamine are identical to those described in the preceding data sheet on monoethylamine.

Precautions in Handling and Storage

The hazards in handling of monomethylamine are due to its toxicity and extreme flammability. Store and use monomethylamine in a well-ventilated area away from heat and all ignition sources such as flame and sparks. Never use flames to detect monomethylamine leaks. Do not use monomethylamine around sparking motors and other non-explosion-proof equipment. Do not store reserve stocks of monomethylamine cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials.

Aside from the above general precautions, the following rules should be observed.

1. Anyone working with monomethylamine should wear rubber gloves, chemical safety goggles, and a rubber or plastic apron.
2. Monomethylamine cylinders should never be heated directly by steam or flames. Uncontrolleld heating of a cylinder can cause the liquid to expand to a point where dangerous hydrostatic pressures will be developed. Any heating should be done in a thermostated water or oil bath. The temperature should not be allowed to exceed 51.7 °C (25 °F). Cylinders of monomethylamine are not equipped with safety devices.
3. Withdrawal of gas should be performed in a well-ventilated area or in a hood.
4. A gas mask approved by NIOSH and showers and an eye bath should be conveniently located in cases of emergency.
5. Weigh monomethylamine cylinders to determine the net contents. The Matheson Model 8510 Cylinder Scale is ideal for this purpose. The tare weight is stamped on all cylinders.
6. Manifolded cylinders of monomethylamine should have check valves at the cylinder outlets to prevent the exchange of material from one cylinder to another causing a cylinder to become overfull.
7. Flames and sparks should not be allowed in the area where monomethylamine is being used.
8. A trap or check valve should be used to prevent suckback of foreign materials into the cylinder. Suckback can cause an extremely corrosive condition to form, aside from the possibility of having a violent reaction take place within the cylinder. Any accidental suckback should be immediately reported to the supplier.
9. Ground all equipment and lines used with monomethylamine.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Never use flames to detect monomethylamine leaks. Leaks can be detected by passing an open bottle or a squeeze bottle containing hydrochloric acid in the vicinity of the suspected leak. Dense white fumes will be formed in the area of the leak. Wet red litmus or phenolphthalein paper will undergo a color change with monomethylamine and are of aid in detecting small leaks.

Leaks which cannot be stopped should be covered with wet rags in order to prevent the atmosphere from becoming contaminated.

Cylinder valves may develop leaks through the packing which can be stopped by tightening up on the packing nut, by turning it counter clockwise. Leaks through the valve outlet that cannot be controlled should be stopped by plugging the outlet with ⅜″ pipe plugs.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-B.

Materials of Construction

Iron and steel are recommended for all equipment coming in contact with monomethylamine. Copper, tin, zinc and their alloys, and aluminum are attacked by moist monomethylamine and should not be used. Piping should be rigid steel except where short connections are required such as between cylinders and manifold or pipe lines. For these applications, a steel reinforced neoprene line is recommended.

For permanent installations, tongue and groove, flanged fittings with lead or asbestos composition gaskets are recommended. In order to reduce maintenance, all joints should be welded wherever possible.

Cylinder and Valve Description

Cylinder valves are made of forged steel and are of the packed type. The valve outlet designated as alternate standard for monomethylamine by the Compressed Gas Association (CGA) is connection No. 240. The thread specifications are ⅜″-18NGT-RH-INT accepting a tapered threaded pipe (see Figure 1 for the drawing and specifications on this valve outlet and its mating connection). Lecture bottles have a special 5/16″-32 threads per inch, female valve outlet.

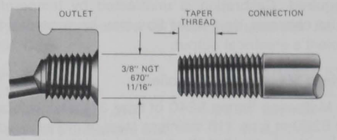


Fig. 1. CONNECTION 240 3/8″-NGT RH INT. IPS accepting Tapered Threaded Pipe

Cylinders containing 15 lb or more monomethylamine are usually equipped with goose neck dip-tubes. Withdrawal of vapor is accomplished by placing the cylinder in its normal vertical position. On occasion, a full cylinder standing in the sun will heat up and cause the liquid to expand and cover the end of the dip-tube. In this case, it is necessary to allow the cylinder to cool before the vapor can be withdrawn or the cylinder should be placed in a horizontal position with the valve outlet facing down.

To withdraw liquid the cylinder should be placed in a horizontal position with the valve outlet facing up.

Matheson

Safety Devices

Since no safety devices are used in monomethylamine cylinders, extra precautions should be used to prevent cylinders from being exposed to heat, which could cause uncontrolled hydrostatic pressure build-up.

Recommended Controls

Automatic Pressure Regulators

Matheson single stage regulator Model 13-240 is recommended for use with monomethylamine. The regulator has an anodized aluminum body, an FEP Teflon on Neoprene diaphragm, a Teflon seat, and type 316 stainless steel internal parts. It has a delivery pressure range of 28-240 kPa (4–35 psig).

Matheson regulator Model 71-240 provides sensitive and very accurate low pressure control. It has an oversize, pancake, aluminum body, a Teflon-faced Butyl rubber diaphragm, a Teflon seat, type 303 stainless steel internal parts, and a delivery pressure range of 3.4–34.5 kPa (0.5–5.0 psig).

Manual Controls

Matheson supplies a stainless steel needle valve, Model 61-240, for direct attachment to the cylinder valve outlet, suitable for manual flow control of the liquid or vapor phase. This valve can be supplied with a hose connection, ¼" tube fitting, or ¼" NPT male or female outlet, stainless steel needle valves, Model 32S or Model 59, are available for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

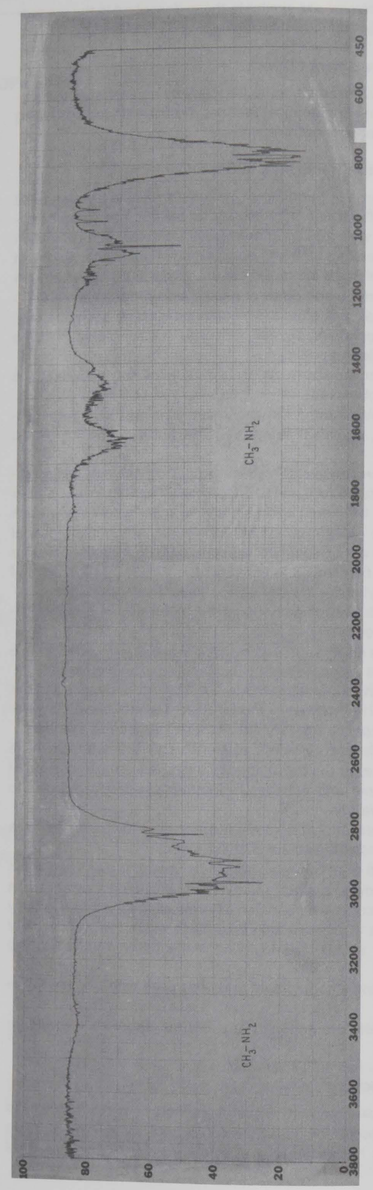
Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ±1.2%.

Shipping Regulations

Monomethylamine is classified by the DOT as a flammable, compressed gas and is shipped with the required "Red Gas Label".



©Sadtler 1972

Reprinted through the courtesy of Sadtler Research Laboratories

Fig. 2. Infrared spectrum of gaseous monomethylamine over the frequency range of 3 800 cm^{-1} to 450 cm^{-1}; 10 cm path length cell, with KBr optics; cell pressure (complete scan) 2.67 kPa (20 mmHg) (6).

Chemical Preparation

Monomethylamine is produced by the interaction of methanol and ammonia over a catalyst at high temperatures. Mono-, di-, and trimethylamines are all produced by this process. Yields are regulated by the conditions employed.

Chemical Properties

Monomethylamine reacts with esters, acid chlorides, or acid anhydrides forming N-methyl amides; with formic acid, formyl derivatives are obtained; with diethy oxalate, N,N¹-dimethyloxamide is formed. Monomethylamine upon treatment with benzenesulfonyl chloride in the presence of aqueous alkali forms N-methylbenzenesulfonamide, soluble in alkaline solution. Nitrous acid and monomethylamine give methanol, nitrogen, and water. With formaldehyde in the presence of alkali, monomethylamine forms either N-hydroxymethylmethylamine or bis(methylamino)methane. In the presence of acids, formaldehyde methylates monomethylamine. Other aliphatic or aromatic aldehydes react with monomethylamine giving Schiff bases. The phenolic hydroxyl in naphthols may be replaced by heating the naphthols with monomethylamine sulfite (Bucherer reaction). Monomethylamine reacts with carbon disulfide forming a methylamine salt of methyldithiocarbamic acid. The unsubstituted amino hydrogens are replaceable by chlorine, bromine, or iodine, either alone or in the presence of alkali. Monomethylamine on warming with chloroform and alkali gives methyl isocyanide (carbylamine reaction). Monomethylamine reacts with substituted or unsubstituted isocyanic and isothiocyanic acids giving substituted ureas and thioureas. Aromatic and heterocylic compounds containing reactive halogen atoms react with monomethylamine forming methylamino derivatives. Monomethylamine reacts with nonmetallic oxy- and sulfochlorides, the monomethylamine replacing one or all of the chlorine atoms, e.g., with S_2Cl_2, $CH_3NHSSNHCH_3$ is formed.

Thermodynamic and Detailed Physical Data

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous monomethylamine.

Vapor Pressure

The vapor pressure of liquid monomethylamine below 101.325 kPa (1 atm) is shown below (3).

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
177.35	0.133	1.33	1
191.85	0.667	6.67	5
199.35	1.333	13.33	10
207.25	2.666	26.66	20
216.25	5.333	53.33	40
221.85	7.999	79.99	60
229.45	13.332	133.32	100
240.75	26.664	266.64	200
253.45	53.329	533.29	400
266.85	101.325	1 013.25	760

The vapor pressure of liquid monomethylamine above 101.325 kPa (1 atm) is listed below (4).

Temperature, °K	Vapor Pressure kPa	bar	atm
266.85	101.325	1.013 25	1
283.25	202.650	2.03	2
309.15	506.625	5.07	5
332.65	1 013.25	10.13	10
360.95	2 026.50	20.27	20
379.45	3 039.75	30.40	30
394.95	4 053.00	40.53	40
406.85	5 066.25	50.66	50
417.75	6 079.50	60.80	60
430.05 (C.T.)	7 457.52	74.58	73.6 (C.P)

For additional vapor pressure data, see Table 1 and Figure 3.

Latent Heat of Vaporization, ΔHv @ 266.82 °K	830.94 kJ/Kg; 198.6 kcal/kg

For additional ΔHv values, see Table 1.

Thermodynamic Data

Thermodynamic properties of saturated monomethylamine are listed in Table 1.

Thermodynamic Properties of Monomethylamine As Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	53.14 J/(mol·°K)
Entropy, S°	243.30 J/(mol·°K)
Enthalpy of Formation, ΔH_f°	−22.97 kJ/mol
Gibbs Energy of Formation, ΔG_f°	32.09 kJ/mol

Thermodynamic Properties of Liquid Monoethylamine @ 25 °C (5)

Entropy	150.21 J/(mol·°K)
Enthalpy of Formation	−47.28 kJ/mol
Gibbs Energy of Formation	35.6 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of monomethylamine, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 51–55, Matheson, Lyndhurst, New Jersey.

[3] *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p. 3–56, McGraw-Hill Book Co., Inc., New York, New York.

[4] **Ibid.**, p. 3–62.

[5] D. D. Wagman, *et al.*, *Selected Values of Chemical Thermodynamic Properties*, *1968*, p. 122, Natl. Bur. Stand. Tech. Note 270-3, U. S. Government Printing Office, Washington, D. C.

[6] *The Sadtler Standard Specta*, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[7] *Refrigerating Data Book*, 5th edition, *1942*, Amer. Soc. Refrig. Engs., New York, New York.

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED MONOMETHYLAMINE (7)

Temperature		Pressure		Entropy J/(mol·°K)		Enthalpy kJ/mol		Latent Heat of Vaporization kJ/mol	Specific Volume m^3/kg		Density kg/m^3	
°K	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
223.15	−58	9.115	0.090	−6.536	118.706	−0.895	27.058	27.953	0.001 345	6.176	743.5	0.161 92
228.15	−49	12.845	0.127	−4.548	118.412	−0.455	27.303	27.758	0.001 355	4.738	738.0	0.211 06
233.15	−40	17.457	0.172	0.000	118.148	0.000	27.556	27.556	0.001 365	3.541	732.6	0.282 41
238.15	−31	23.511	0.232	1.923	116.705	0.455	27.794	27.339	0.001 375	2.725	727.3	0.366 97
243.15	−22	31.378	0.310	3.820	115.354	0.917	28.040	27.123	0.001 386	2.033	721.5	0.491 88
248.15	−13	41.506	0.140	5.718	114.093	1.379	28.271	26.892	0.001 397	1.576	715.8	0.634 52
253.15	−4	53.641	0.529	7.615	112.911	1.855	28.516	26.661	0.001 408	1.239	710.2	0.807 10
258.15	+5	69.154	0.683	9.499	111.793	2.353	28.769	26.416	0.001 420	0.970	704.2	1.030 9
263.14	14	87.357	0.862	11.357	110.728	2.808	28.964	26.156	0.001 432	0.778	698.3	1.285 3
268.15	23	110.247	1.088	13.190	109.714	3.292	29.187	25.895	0.001 444	0.625	692.5	1.600 0
273.15	32	136.723	1.349	14.996	108.752	3.783	29.404	25.621	0.001 456	0.515	686.8	1.914 7
278.15	41	168.853	1.666	16.789	107.856	4.274	29.606	25.332	0.001 469	0.424	680.7	2.358 5
283.15	50	205.946	2.033	18.569	107.011	4.772	29.823	25.051	0.001 482	0.353	674.8	2.832 9
288.15	59	250.073	2.468	20.324	106.231	5.277	30.032	24.755	0.001 496	0.295	668.4	3.389 8
293.15	68	300.060	2.961	22.065	105.452	5.790	30.234	24.444	0.001 510	0.249	662.3	4.016 1
298.15	77	358.941	3.542	23.793	104.737	6.302	30.436	24.134	0.001 524	0.211	656.2	4.739 3
303.15	86	424.234	4.187	25.509	104.061	6.822	30.639	23.817	0.001 538	0.185	650.2	5.405 4
308.15	95	500.628	4.941	27.237	103.438	7.356	30.841	23.485	0.001 563	0.155	639.8	6.451 6
313.15	104	574.678	5.672	28.952	102.853	7.891	31.036	23.145	0.001 569	0.134	637.3	7.462 7
318.15	113	680.926	6.720	30.667	102.307	8.439	31.231	22.792	0.001 585	0.117	630.9	8.547 0
323.15	122	786.002	7.757	32.396	101.813	8.995	31.447	22.452	0.001 602	0.102	624.2	9.803 9

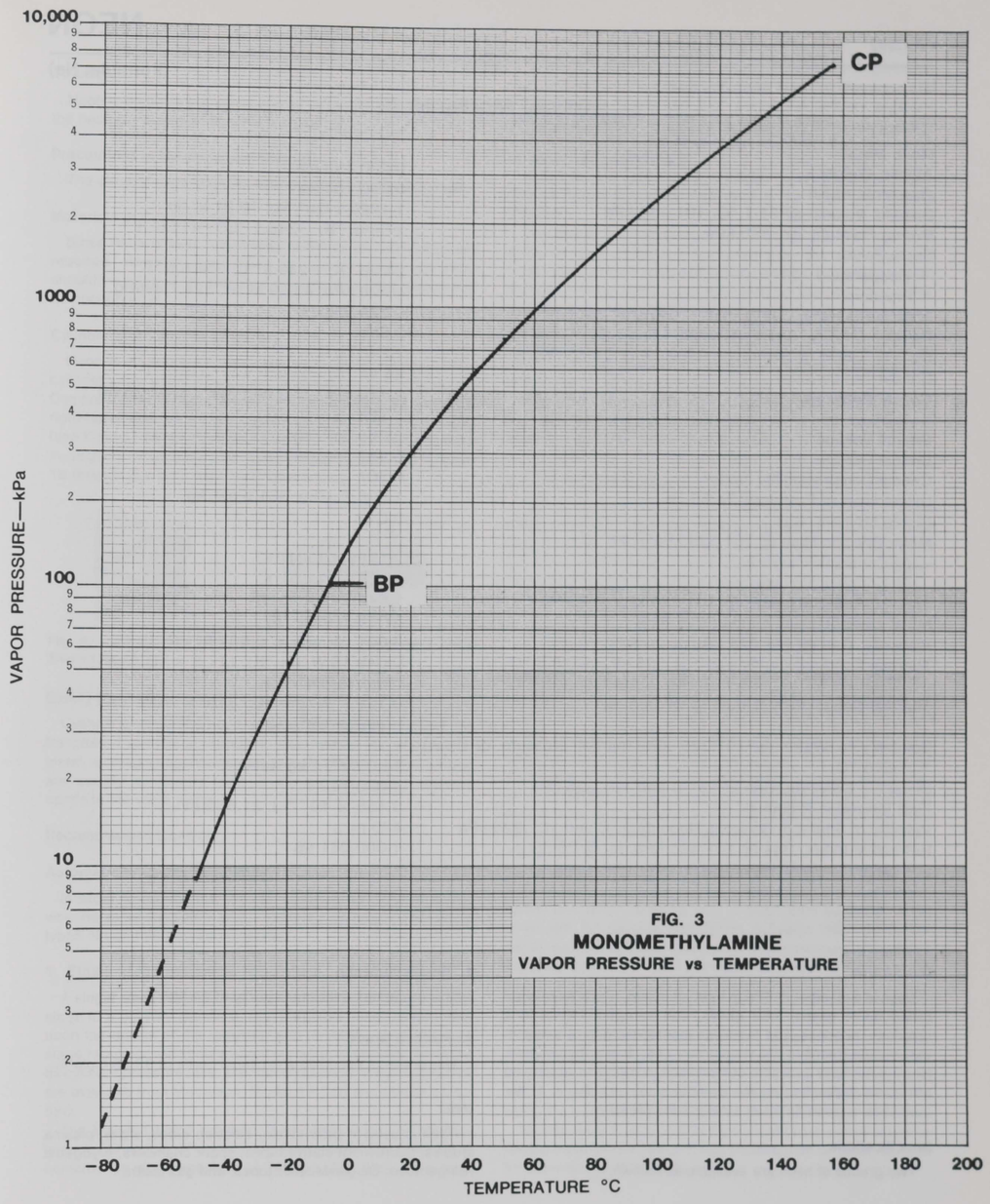


FIG. 3
MONOMETHYLAMINE
VAPOR PRESSURE vs TEMPERATURE

(Formula: Ne)

PHYSICAL PROPERTIES (1)

Molar Mass	
Atomic Weight	0.020 183 kg
One Mole of Ne	0.020 183 kg
Specific Volume @ 21.1 °C, 101.325 kPa	1 1990.0 dm^3/kg; 19.21 ft^3/lb
Boiling Point @ 101.325 kPa	27.066 °K; −246.1 °C; −411.0 °F
Triple Point	
Temperature	24.56 °K; −248.6 °C; −415.5 °F
Pressure	43.29 kPa; 432.9 mbar; 324.7 mmHg
Absolute Density, Gas @ 101.325 kPa @ 25 °C	0.824 5 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (air = 1)	0.696
Density, Liquid @ Saturation Pressure @ 24.55 °K	1.248 kg/l
Critical Temperature	44.44 °K; −228.7 °C; -379.7 °F
Critical Pressure	2 720 kPa; 27.2 bar; 394.7 psia; 26.86 atm
Critical Volume	2.068 dm^3/kg
Critical Density	0.483 5 kg/dm^3
Critical Compressibility Factor	0.307
Latent Heat of Fusion @ 24.56 °K	1 596.2 J/kg; 381.5 cal/kg
Dipole Moment, Gas	0 C·m
Molar Specific Heat @ 101.325 kPa @ 25 °C	
@ Constant Pressure	20.786 J/(mol·°K)
@ Constant Volume	12.659 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.642
Molar Specific Heat, Liquid @ 26.8 °K	37.15 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 26.8 °C	0.031 81 mPa·s; 0.031 81 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 26.8 °C	0.049 16 W/(m·°K); 117.5 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ 27.066 °K	0.129 7 W/(m·°K); 310 × 10^{-6} cal·cm/(s·cm^2·°C)
Solubility In Water @ 101.325 kPa (partial pressure of neon) @ 0 °C	14.0 cm^3/1 kg water
Dielectric Constant, Gas @ 25 °C and 101.325 kPa	1.000 122 9
First Ionization Potential	3.455 × 10^{-18} J; 21.563 eV
Velocity of Sound In Gaseous Neon @ 0 °C and 101.325 kPa	435 m/s
Refractive Index, Gas @ 101.325 kPa, n_D @ 25 °C	1.000 061 46

Description

Neon is a member of Group VIIIA elements, which have been called noble gases, inert gases, and aerogens. Neon is a colorless, odorless, and tasteless monatomic gas. It exists in very minute traces in the atmosphere (18.18 ppm by volume). Neon is normally available compressed in cylinders at varying pressures depending on the cylinder size, and also in 1 liter quantities in glass flasks at atmospheric pressure.

Specifications

Two grades of neon are available as follows:

1. Research Grade

This grade has a minimum purity of 99.999 mole %.

2. Purified Grade

This grade of neon has a minimum purity of 99.99 mole %.

Uses

Neon is used in glow lamps, electron tubes, signs, plasma studies, fluorescent starter tubes, spark chambers, cryogenic refrigeration, Geiger-Mueller tubes, and gas lasers.

Toxicity

Neon is nontoxic but can act as an asphyxiant by displacing the necessary amount of air to support life.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Materials of Construction

Since neon is inert, no special materials of contruction are required. However, any piping or vessels containing neon should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

Neon is packaged in DOT approved, steel cylinders. The cylinder valve outlet designated as standard, No. 580, by the Compressed Gas Association (CGA) has a 0.965 inch diameter right-hand internal thread accepting a bullet-shaped nipple (see Figure 1 for an illustration). Lecture bottles have a special 5/16 inch-32 threads per inch, female valve outlet and a 9/16 inch-18 threads per inch, male dual valve outlet.

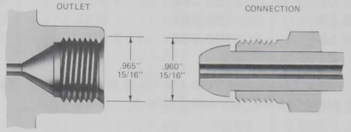


Fig. 1. CONNECTION 580 .965"-14 RH INT. accepting a Bullet Shaped Nipple

Safety Devices

Cylinders containing neon have safety devices of either the frangible disc type or frangible disc backed up with fusible metal, melting at approximately 212 °F. These safety devices are usually an integral part of the cylinder valve, situated opposite the valve outlet.

Recommended Controls

Automatic Pressure Regulators

In order to reduce the cylinder pressure of neon to a safe working value consistent with a system's design, the following types of controls are recommended.

1. Single Stage Automatic Regulators

A single stage regulator will reduce cylinder pressure in one stage to a delivery pressure, in a particular range, depending upon the design of the regulator and its spring load. A single stage regulator will show a slight variation in delivery pressure as cylinder pressure falls. The following single stage regulators are available from Matheson: Model 19-580 and Model 3500-580.

The Model 19-580 regulator is recommended for applications requiring low diffusion and leakage rates. It is of all brass construction with diaphragm of German silver alloy (65% copper, 17% zinc, 18% nickel) with nylon seat and aluminum and nylon gaskets. It has two 2½" gauges, a delivery pressure gauge of 0-690 kPa (0-100 psig) and a tank pressure gauge of 0-20 680 kPa (0-3 000 psig). It has a delivery pressure range of 28-345 kPa (4-50 psig).

A helium leak rate certification can be obtained optionally. The maximum acceptable rate is 2 × 10^{-9} cm^3 per second inboard.

The Model 3500-580 regulator is constructed of type 316 stainless steel. It has a Teflon-lined type 301 stainless steel diaphragm, a Kel-F seat, and Teflon gaskets. It is provided with a diaphragm packless outlet valve with ¼" Gyrolok tube fitting, and stainless steel delivery pressure and cylinder pressure gauges. There are no rubber parts. It has a delivery pressure range of 28-520 kPa (4-75 psig). A helium leak rate certification can be obtained optionally. The maximum acceptable leak rate is 2 × 10^{-10} cm^3 per second inboard.

Regulator Model 3320 with a delivery pressure range of 28-410 kPa (4-60 psig) is recommended for use with lecture bottles containing Purified Grade neon.

2. Two Stage Regulators

This type of regulator performs the same function as a single stage regulator. However, greater accuracy and control of delivery pressure is maintained, and the delivery pressure does not vary as the cylinder pressure falls. The following two stage regulators are available from Matheson:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
3800-580	28–620	0.28–6.2	4–90
3104-580	28–690	0.28–6.9	4–100

The Model 3800-580 regulator is constructed of type 316 stainless steel. It is provided with a type 316 stainless steel diaphragm, Kel-F seat, Kel-F and Teflon gaskets, and a diaphragm packless outlet valve with ¼" Gyrolok tube fitting. A helium leak rate certification can be obtained optionally. The maximum acceptable leak rate is 2 × 10^{-9} cm^3 per second inboard.

The Model 3104-580 regulator is constructed of brass. It is provided with a type 302 stainless steel diaphragm, Kel-F seat, Teflon and nylon gaskets, and a diaphragm packless outlet valve with ¼" Gyrolok tube fitting. A helium leak rate certification can be obtained optionally. The maximum acceptable leak rate is 2 × 10^{-9} cm^3 per second inboard.

Manual Controls

Model 4351-580 of chrome-plated brass construction with a diaphragm packless valve is recommended for use with neon. This valve should be used only as a manual flow-control and not as a pressure control, since dangerous pressure can develop if a line becomes plugged or the system itself is closed.

Needle valve Model 30AR of chromed brass construction or needle valve Model 31B of brass construction is recommended for use with Purified Grade neon.

Flowmeters

Matheson Series 7600 laboratory brass or stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass or stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes. Flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ±1.2%.

Shipping Regulations

Neon is shipped in high pressure steel cylinders as a nonflammable compressed gas, taking a DOT "Green Label".

Commercial Preparation

Neon is available only from the atmosphere, and is obtained by the liquefaction and fractionation of air.

Chemical Properties

Neon is chemically inert under all normal conditions.

Thermodynamic and Detailed Physical Data

Molecular Structure

The neon atom has a valence shell of eight electrons, which is a closed octet. The closed shell is extremely stable and results in neon being inert chemically. Neon has an atomic radius of 1.60 Å (1.60×10^{-10} m).

Vapor Pressure

The vapor pressure of liquid neon in the range 23.86–29.55 °K is represented by the following Antoine vapor pressure equation (2):

$$\log_{10} p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.084 44, 78.380, and 270.550, respectively.

Some calculated vapor pressures are shown below.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
23.86	33.331	333	250
24.33	39.997	400	300
25.108	53.329	533	400
25.572	66.661	667	500
26.306	79.993	800	600
26.796	93.326	933	700
27.066	101.325	1 013.25	760
27.237	106.658	1 067	800
27.640	119.990	1 200	900
28.01	133.322	1 333	1 000
28.68	159.987	1 600	1 200
29.55	199.984	2 000	1 500

For vapor pressures from the triple point (24.55 °K) to the critical point (44.44 °K), see Table 1.

Latent Heat of Vaporization, ΔHv @ 27.066 °K 8 893.3 J/kg (429.0 cal/mol)

For additional ΔHv values, see Table 1.

Thermodynamic Data

Thermodynamic properties of saturated neon and real gas neon are shown in Tables 1 and 2, respectively. Compressibility data are shown in Table 3.

Thermodynamic Properties of Neon As Ideal Gas @ 25 °C (3)

Heat Capacity, C_p°	20.786 J/(mol·°K)
Entropy, S°	146.225 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_0^\circ)/298$	−125.438 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	6.197 6 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of neon, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] B. J. Zwolinski, *et al.*, *Selected Values of Chemical Compounds, 1968*, Volume 1, Thermodynamic Research Center, Texas A & M University, College Station, Texas.

[3] *Argon, Helium and the Rare Gases*, G. A. Cook, editor, *1961*, Volume 1, p. 293, Interscience Publishers, Inc., New York, New York.

[4] *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p. 3–182, McGraw-Hill Book Co., Inc., New York, New York.

[5] See reference 3, p. 296.

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED NEON (4)

Temperature °K	Temperature °F	Pressure kPa	Pressure atm	Entropy kJ/(kg·°K) Liquid	Entropy kJ/(kg·°K) Vapor	Enthalpy kJ/kg Liquid	Enthalpy kJ/kg Vapor	Latent Heat of Vaporization kJ/kg	Specific Volume dm^3/kg Liquid	Specific Volume dm^3/kg Vapor	Density kg/dm^3 Liquid	Density kg/dm^3 Vapor
24.54	−415.50	43.266	0.427	0.000	3.633	0.0	89.2	89.2	0.801	227.9	1.248	0.004 39
26	−412.87	71.839	0.709	0.105	3.475	2.7	90.3	87.6	0.817	143.6	1.224	0.006 96
28	−409.27	132.128	1.304	0.245	3.287	6.5	91.7	85.2	0.841	82.35	1.189	0.012 14
30	−405.67	223.827	2.209	0.381	3.122	10.6	92.8	82.2	0.869	50.62	1.151	0.019 76
32	−402.07	355.245	3.506	0.516	2.973	14.9	93.5	78.6	0.900	32.77	1.111	0.030 52
34	−398.47	535.199	5.282	0.650	2.834	19.4	93.7	74.3	0.938	22.02	1.066	0.045 41
36	−394.87	772.806	7.627	0.786	2.697	24.5	93.2	68.7	0.982	15.15	1.018	0.066 01
38	−391.27	1 078.10	10.64	0.929	2.556	30.0	91.9	61.9	1.038	10.53	0.963	0.094 97
40	−387.67	1 462.12	14.43	1.080	2.403	36.4	89.3	52.9	1.113	7.293	0.898	0.137 12
42	−384.07	1 938.35	19.13	1.249	2.232	43.8	85.1	41.3	1.226	4.960	0.816	0.201 61
44	−380.47	2 521.98	24.89	1.481	2.038	54.7	79.1	24.4	1.474	3.238	0.678	0.308 83
44.4	−379.75	2 653.70	26.19						2.07	2.07	0.483	0.483

Table 2. ENTHALPY DIFFERENCE ($H_T^\circ - H_0^\circ$), kJ/mol, AND ENTROPY (S), J/(mol•°K) OF REAL GAS NEON (5)

Pressure kPa	atm		Temperature, °K 50	75	100	125	150	175	200	225	250	275	300
101.325	1	H	1.027 2	1.553 5	2.076 1	2.596 6	3.116 7	3.636 3	4.157 2	4.667 3	5.196 9	5.717 0	6.235 8
		S	108.939	117.483	123.491	128.143	131.938	135.139	137.917	140.365	142.561	144.536	146.348
1 013.250	10	H	0.905 8	1.502 9	2.047 2	2.578 6	3.105 8	3.630 0	4.152 6	4.675 2	5.196 9	5.717 9	6.238 3
		S	88.107	97.839	104.110	108.859	112.700	115.934	118.725	121.190	123.382	125.369	127.189
2 026.500	20	H	0.756 5	1.445 6	2.015 9	2.559 8	3.093 2	3.622 1	4.149 3	4.673 5	5.196 9	5.719 5	6.242 1
		S	80.195	91.508	89.081	102.939	106.834	110.098	112.914	115.340	117.591	119.579	121.395
4 053.000	40	H	0.452 3	1.330 5	1.954 3	2.523 0	3.071 5	3.610 4	4.143 0	4.672 7	5.199 9	5.725 8	6.250 1
		S	70.049	84.592	91.797	96.876	100.880	104.198	107.052	109.541	111.763	113.767	115.596
6 079.500	60	H	0.319 2	1.221 3	1.897 9	2.490 7	3.052 6	3.600 3	4.139 2	4.673 5	5.204 9	5.733 8	6.260 9
		S	65.459	80.094	87.918	93.215	97.320	100.701	103.579	106.098	108.336	110.353	112.186
10 132.500	100	H	0.389 5	1.022 6	1.797 9	2.435 9	3.023 8	3.588 6	4.140 1	4.682 3	5.220 4	5.754 7	6.286 0
		S	64.275	73.743	82.730	88.433	92.730	96.211	99.152	101.717	103.985	106.014	107.868
14 185.500	140	H	0.519 2	0.853 5	1.713 3	2.393 7	3.004 9	3.585 3	4.147 2	4.698 6	5.243 0	5.781 5	6.317 8
		S	64.676	69.086	79.061	85.140	89.609	93.190	96.194	98.793	101.085	103.136	105.010
18 238.500	180	H	0.643 9	0.667 4	1.640 5	2.359 4	2.994 1	3.588 6	4.161 8	4.720 4	5.270 6	5.814 1	6.353 8
		S	65.09	64.940	76.153	82.596	87.228	90.897	93.956	96.588	98.910	100.981	102.859
20 265.000	200	H	0.704 2	0.614 2	1.607 5	2.344 7	2.990 7	3.592 4	4.170 6	4.732 9	5.286 1	5.832 1	6.373 5
		S	65.291	63.354	74.885	81.488	86.211	89.914	93.010	95.655	97.993	100.069	101.952

Table 3. COMPRESSIBILITY FACTORS FOR NEON

Pressure kPa	Temperature, °K 266.48	272.04	277.59	283.15	288.71	294.26	299.82	305.37	310.93	316.48	322.04
137.895	1.000 6	1.000 6	1.000 6	1.000 6	1.000 6	1.000 6	1.000 6	1.000 6	1.000 6	1.000 6	1.000 6
275.790	1.001 2	1.001 2	1.001 2	1.001 2	1.001 2	1.001 2	1.001 2	1.001 1	1.001 1	1.001 1	1.001 1
413.685	1.001 8	1.001 8	1.001 8	1.001 8	1.001 7	1.001 7	1.001 7	1.001 7	1.001 7	1.001 7	1.001 7
689.476	1.002 9	1.002 9	1.002 9	1.002 9	1.002 9	1.002 9	1.002 9	1.002 9	1.002 9	1.002 8	1.002 8
1 378.95	1.005 9	1.005 9	1.005 9	1.005 9	1.005 9	1.005 8	1.005 8	1.005 8	1.005 7	1.005 7	1.005 7
2 757.90	1.011 9	1.011 9	1.011 9	1.011 8	1.011 8	1.011 7	1.011 7	1.011 6	1.011 6	1.011 5	1.011 4
4 136.85	1.018 0	1.018 0	1.018 0	1.017 9	1.017 8	1.017 7	1.017 6	1.017 5	1.017 4	1.017 3	1.017 2
5 515.81	1.024 3	1.024 2	1.024 1	1.024 0	1.023 9	1.023 8	1.023 7	1.023 5	1.023 4	1.023 2	1.023 1
6 894.76	1.030 6	1.030 5	1.030 3	1.030 2	1.030 1	1.029 9	1.029 7	1.029 6	1.029 4	1.029 2	1.029 0
8 273.71	1.037 0	1.036 8	1.036 7	1.036 5	1.036 3	1.036 1	1.035 9	1.035 7	1.035 4	1.035 2	1.034 9
11 031.6	1.050 0	1.049 8	1.049 5	1.049 2	1.049 0	1.048 7	1.048 3	1.048 0	1.047 7	1.047 3	1.047 0
13 789.5	1.063 3	1.063 0	1.062 6	1.062 3	1.061 9	1.061 5	1.061 0	1.060 6	1.060 1	1.059 7	1.059 2
17 236.9	1.080 4	1.079 9	1.079 4	1.078 9	1.078 3	1.077 7	1.077 2	1.076 6	1.076 0	1.075 3	1.074 7
20 684.3	1.097 9	1.097 2	1.096 5	1.095 8	1.095 1	1.094 3	1.093 6	1.092 8	1.092 0	1.091 2	1.090 5

NICKEL CARBONYL

(Synonym: Nickel Tetracarbonyl)
(Formula: $Ni(CO)_4$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.170 752 kg
One Mole of $Ni(CO)_4$	0.170 752 kg
Vapor Pressure @ 20 °C	42.00 kPa; 420.0 mbar; 315 mmHg
Boiling Point @ 101.325 kPa	315.60 °K; 42.4 °C; 108.4 °F
Melting Point	253.86 °K; −19.3 °C; −2.7 °F
Absolute Density, Gas @ 101.325 kPa @ 50 °C	6.531 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 50 °C (Air = 1)	5.95
Density, Liquid @ 25 °C	1.30 kg/l
Critical Temperature	473.15 °K; 200.0 °C; 390.0 °F
Critical Pressure	3 040 kPa; 30.4 bar; 440.9 psia; 30 atm
Critical Volume	2.174 dm^3/kg
Critical Density	0.46 kg/dm^3
Critical Compressibility Factor	0.287
Latent Heat of Fusion @ −19.3 °C	13.786 kJ/mol; 3.295 kcal/mol
Lower Flammability in Air	2% (by volume)
Viscosity, Liquid @ 25 °C	0.212 mPa·s; 0.212 cP
Molar Specific Heat, Liquid @ 26.8 °C	204.76 J/(mol·°K)
Surface Tension @ 20 °C	15.88 mN/m; 15.88 dyn/cm
Solubility In Water @ 9.8 °C	0.017 6 kg/100 by water
Trouton Constant	20.6
Electrical Conductivity @ 25 °C	$1 \times 10^{-9}\ \Omega^{-1}$/cm
Ignition (Explosion) Temperature	333.15 °K; 60 °C; 140 °F
Heat of Combustion, Liquid @ 25 °C	−1 180.7 kJ/mol; −2.82.2 kcal/mol

Description

Nickel carbonyl is a colorless, flammable, mobile liquid with a characteristic ordor at room temperature and atmospheric pressure. Its vapor is highly toxic. It is shipped as a liquid in cylinders pressurized to 103 kPa (15 psig) at 20 °C.

Specifications

There are no minimum purity specifications for nickel carbonyl. Since it is used in the Mond process for refining crude nickel to obtain nickel of high purity, it is considered to have a purity of above 99.9%.

Uses

Nickel carbonyl is used in the Mond process to obtain nickel of high purity, to obtain metallic mirrors, and to coat objects with a thin film of nickel. It is an effective catalyst in the carbonylation reaction (reaction of olefins, acetylenes, haloacetylenes, alcohols, and aryl halides with carbon monoxide).

Effects In Man and Toxicity (2)

Symptoms of nickel carbonyl poisoning depend on the concentration of the vapor, duration of exposure, and individual susceptibility. Acute poisoning is of two types, initial and delayed, which may be subdivided into groups of mild and severe cases. The delayed stage occurs 12–36 hours after the initial stage.

Initial symptoms of mild cases are giddiness and slight frontal headache. Severe cases complain of nausea, vomiting, tightness in the chest, weakness, and respiratory distress.

Respiration is the best guide to the severity of the case since the rate tends to increase according to the amount of damage to the respiratory system. A useful guide is the pulse-respiration ratio which is normally 4:1. Any case with a ratio under 3:1 should be watched carefully. Other guides to the severity of the case may be obtained by analysis of the urine or blood for nickel.

Cancer of the lung and nose has long been considered the long term effect in nickel refinery (Mond Process) workers.

The lowest lethal concentration in humans by inhalation is reported to be 57 ppm/30 minutes. The LC_{50} in the rat by inhalation is stated to be 240 × 10^{-6} kg (240 mg)/m^3/30 minutes.

The odor of nickel carbonyl is not adequate as a warning of the presence of dangerous concentrations of vapor.

The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 0.05 ppm (0.35 mg/m^3) for nickel carbonyl.

First Aid Treatment (2)

Remove the victim immediately from the contaminated area (rescuers should don adequate protective equipment for this). Remove the outer clothing of the victim and wrap him in blankets, put him in bed and keep him warm. If the victim is breathing, administer a mixture of 95% oxygen and 5% carbon dioxide. If the victim is not breathing, start artificial respiration at once, with simultaneous administration of the oxygen-carbon dioxide mixture. The inhalation is continued 15 to 30 minutes after spontaneous breathing returns. An 8-hour collection of urine is begun for nickel analysis (or the amount of nickel in the blood determined). Summon a physician as soon as possible, notifying him of the nature of the accident and the exact location of the victim.

Suggestions for Medical Treatment (2)

The nickel concentration in the initial 8-hour collection of urine (or the nickel concentration in the blood) is a valuable aid in classifying patients. If the patient's exposure to nickel carbonyl has been severe and typical initial symptoms appear, then Dithiocarb (sodium diethyldithiocarbamate trihydrate) therapy may be instituted immediately, either orally or, in critical cases, by parenteral routes. If there is any doubt regarding the severity of exposure or if the symptoms are minimal, decisions regarding therapy may be deferred until the analysis of the urine for nickel is available.

If the initial 8-hour specimen of urine has a nickel concentration of less than 10×10^{-6} kg/100 ml (or below 10 ppm nickel in the blood), the exposure may be classified as mild. In such cases, it is probable that delayed symptoms will either not develop or will be minimal. It is advisable, however, to observe the patient for 24 hours. Analyses of the nickel concentration in urine should be made daily, until the concentration has returned to the normal range, the upper limit of which is 3.0×10^{-6} kg/100 ml. If severe delayed symptoms develop unexpectedly, the patient should be hospitalized and given Dithiocarb immediately.

If the nickel concentration in the initial 8-hour specimen of urine is above 10 but less than 50×10^{-6} kg/100 ml (or 10–20 ppm nickel in the blood), the exposure may be classified as moderately severe. Since delayed symptoms frequently develop in these patients, they should remain at rest for at least a week. Dithiocarb may be administered orally in doses of 0.5 gram 3 or 4 times daily together with 0.5×10^{-4} kg sodium bicarbonate and a full glass of water. Dithiocarb therapy is continued until the patient is free of symptoms and the concentration of nickel in the urine is less than 10×10^{-6} kg/100 ml.

If the nickel concentration in the initial 8-hour specimen of urine is above 50×10^{-6} kg/100 ml (or above 20 ppm nickel in the blood), the exposure may be classified as severe. These patients are apt to be seriously ill and require hospitalization. Most of these patients can be maintained with oral Dithiocarb as outlined for the moderately severe group. However, if the patient's condition is critical, it is suggested that Dithiocarb be administered parenterally in an initial dosage of 25×10^{-6} kg per kg of body weight and that the total amount during 24 hours be limited to 100×10^{-6} kg per kg of body weight the Dithiocarb solution for injection is prepared by adding 10 ml of a sterile solution of phosphate buffer (0.5×10^{-4} kg monosodium phosphate/100 ml) to 1×10^{-3} kg powdered Dithiocarb in a sterile ampul; the solution contains 100×10^{-6} kg Dithiocarb/ml. With continued Dithiocarb therapy, the concentration of nickel in the urine gradually decreases and reaches approximately normal levels within 16 days after exposure.

Patients receiving Dithiocarb should abstain from alcoholic beverages.

Precautions in Handling and Storage

The major hazards resulting from the handling of nickel carbonyl stem from its extreme toxicity and its flammability. The gas should, therefore, be handled only in well-ventilated areas, preferably in an adequately designed hood with forced ventilation to provide for removal of the heavy vapors of nickel carbonyl which are about 6 times as dense as air. Whenever possible, nickel carbonyl should be handled outside in the open air, with the cylinder below the level of the face and with the handler standing favorably to the wind. The handler should use an air respirator. If nickel carbonyl is handled inside a building, all windows should be opened and exhaust fans started and the person handling the liquid should use an air-line respirator. Ordinary gas masks containing charcoal absorbents (preferably one approved by NIOSH) will give protection, provided the concentration of nickel carbonyl is less than 10 ppm. Above this concentration, an air-line respirator is required. Extra air respirators should be kept in convenient locations for use in emergencies. When working with nickel carbonyl, it is preferable to use a closed system. Nickel carbonyl should never be handled near an open flame, hot surface, or sparks.

In addition, the general rules listed in Appendix I should be observed, as well as the following ones.

1. Do not store reserve stocks of nickel carbonyl with cylinders containing oxygen, or other highly oxidizing or flammable materials.
2. Handling of nickel carbonyl should be under the supervision of a qualified chemist who is familiar with its physical and chemical properties.
3. To remove nickel carbonyl from a cylinder, first attach an appropriate needle valve (see Recommended Controls) to the cylinder valve outlet. Make sure this valve is closed. To obtain a liquid sample, place the cylinder in a hood or attach a metal line to the cylinder and extend it into a hood. Invert the cylinder with an inverter, such as Matheson Model 509 inverter, or clamp in an inverted position. Connect the appropriate tubing to the equipment or direct the tubing to a measuring device (narrow necked beaker, volumetric cylinder, Erlenmeyer flask, etc.). If the sampling is made into a measuring device, attach a flexible plastic hose to the end of the line and insert into measuring device (in hood). Purge the device with an inert gas. Open needle valve slowly until the desired quantity of liquid is obtained. Close the needle valve and then the cylinder valve. Remove needle valve and flush with inert gas (in hood or well-ventilated area) when not in use for extended periods. Disassembly of valves and lines can be hazardous due to liquid remaining in lines. All such work should be done with good ventilation, or with the operator utilizing an air supplied mask.
4. Ground all lines and equipment used with nickel carbonyl.

Leak Detection

Systems designed to contain nickel carbonyl should be pretested for leaks with an inert gas.

Materials of Construction

Nickel carbonyl itself is not corrosive, although some nickel plating of the metal used may occur.

When it is used in organic carbonylation reactions, usually in association with carbon monoxide, corrosion definitely becomes a problem, particularly at elevated temperatures and high carbon monoxide pressures. Copper or glass-lined equipment would probably be suitable under these reaction conditions.

Cylinder and Valve Description

Nickel carbonyl is shipped in D.O.T. approved steel cylinders with a cylinder valve of brass with Compressed Gas Association (CGA) connection No. 320. This valve outlet is 0.825″ in diameter with right-hand external threads, with a flat seat and used with a washer to seal (see Figure 1 for illustration of this outlet and mating connection). Lecture bottles have a 5/16″-32 threads per inch, female outlet.

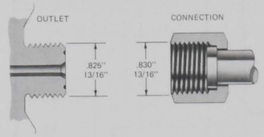


Fig. 1 CONNECTION 320 .825″-14 RH EXT. used with Flat Seat and Washer

Safety Devices

Cylinders of nickel carbonyl pressurized with carbon monoxide have a safety device incorporated in the cylinder valve. This device consists of a frangible disc backed up with a fusible metal.

Recommended Controls

Manual needle valve Model 50A-320, of chrome plated brass, is available for direct connection to the cylinder valve outlet and will provide adequate flow control. This valve is equipped with a ¼″ tube fitting outlet connection. Brass needle valve Model 58 is recommended for use with lecture bottles.

Shipping Regulations

Nickel carbonyl is classified by the DOT as a flammable liquid and is shipped with the required "Red Label".

Commercial Preparation

In the Mond process finely divided, metallic nickel is treated with carbon monoxide at about 60 °C to form nickel carbonyl gas, leaving the impurities, including cobalt, as a solid residue. Subsequent heating of the nickel carbonyl gas at about 180 °C forms cobalt-free nickel, about 99.9% purity, and carbon monoxide, which is recirculated.

Chemical Properties

In nickel carbonyl, the 4 carbonyl groups form a tetrahedral arrangement and act as electron donors to the central nickel atom, which has a valence number of zero. Its properties reflect this unusual coordination structure. Thermodynamic data show that unless the pressure of carbon monoxide approximates 1 atmosphere, nickel carbonyl is almost completely dissociated. The decomposition is fairly rapid but not instantaneous. Nickel carbonyl is only slilghtly soluble in water (18×10^{-6} kg/0.1 kg water at 9.8 °C), but is highly soluble in organic solvents, such as ethanol, ether, benzene, and chloroform. It reacts slowly with hydrochloric acid and sulfuric acid, and vigorously with nitric acid and the halogens to form the corresponding bivalent nickel salts. For synthesis of α,β-unsaturated carboxylic acids, allenic acids, saturated aliphatic carboxylic acids, aryl carboxylic acids, formamides, ureas, etc., by direct carbonylation reactions with nickel carbonyl, consult the review article by Bird (3).

Thermodynamic and Detailed Physical Data

Molecular Structure

The tetrahedral nickel carbonyl molecule has T_d symmetry and a symmetry number of twelve, with the following bond distances: Ni-C 1.82 Å (1.82×10^{-10} m); C-O 1.15 Å (1.15×10^{-10} m).

Infrared Spectrum

See Figure 2 for the infrared spectrum of nickel carbonyl vapor.

Vapor Pressure (4)

The vapor pressure of liquid nickel carbonyl up to 101.325 kPa (1 atm) is shown below.

Temperature, °K	Vapor Pressure		
	kPa	mbar	mmHg
250.15	5.332 9	53.3	40
257.25	7.999 3	80.0	60
267.15	13.332 2	133.3	100
281.95	26.664 5	266.6	200
298.95	53.328 9	533.3	400
315.65	101.325 0	1 013.25	760

See Figure 3 for the vapor pressure curve up to 101.325 kPa.

Latent Heat of Vaporization, ΔHv

Temperature, °C	ΔHv, kJ/mol
0	32.1
25	30.5
42.4	29.3

Thermodynamic Properties of Nickel Carbonyl As Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	137.24 J/(mol·°K)
Entropy, S°	405.85 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - E_0^\circ)/298$	−307.11 J/(mol·°K)

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of nickel carbonyl, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, and A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 106–110, Matheson, Lyndhurst, New Jersey.

[3] C. W. Bird, Chem. Rev. 62, 283 (1962).

[4] *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p. 3–47, McGraw-Hill Book Co., Inc., New York, New York.

[5] B. L. Crawford and P. C. Cross, *J. Chem. Phys.* 6, 525–530 (1938).

[6] L. H. Jones, *J. Chem. Phys.* 28, 1205–1219 (1958).

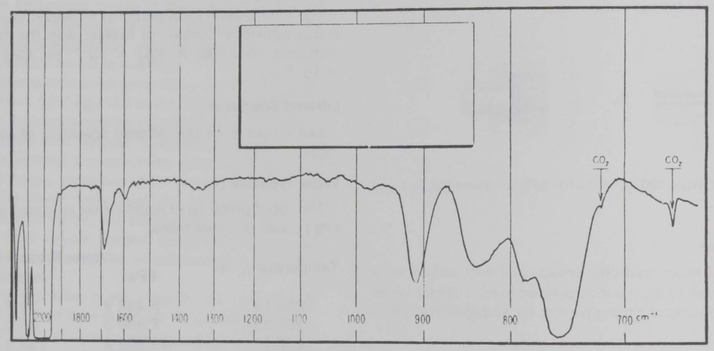


Fig. 2. Infrared spectrum of nickel carbonyl vapor at room temperature; NaCl prism; 10 cm path length; cell pressure: 39.997 kPa (300 mmHg) (6).

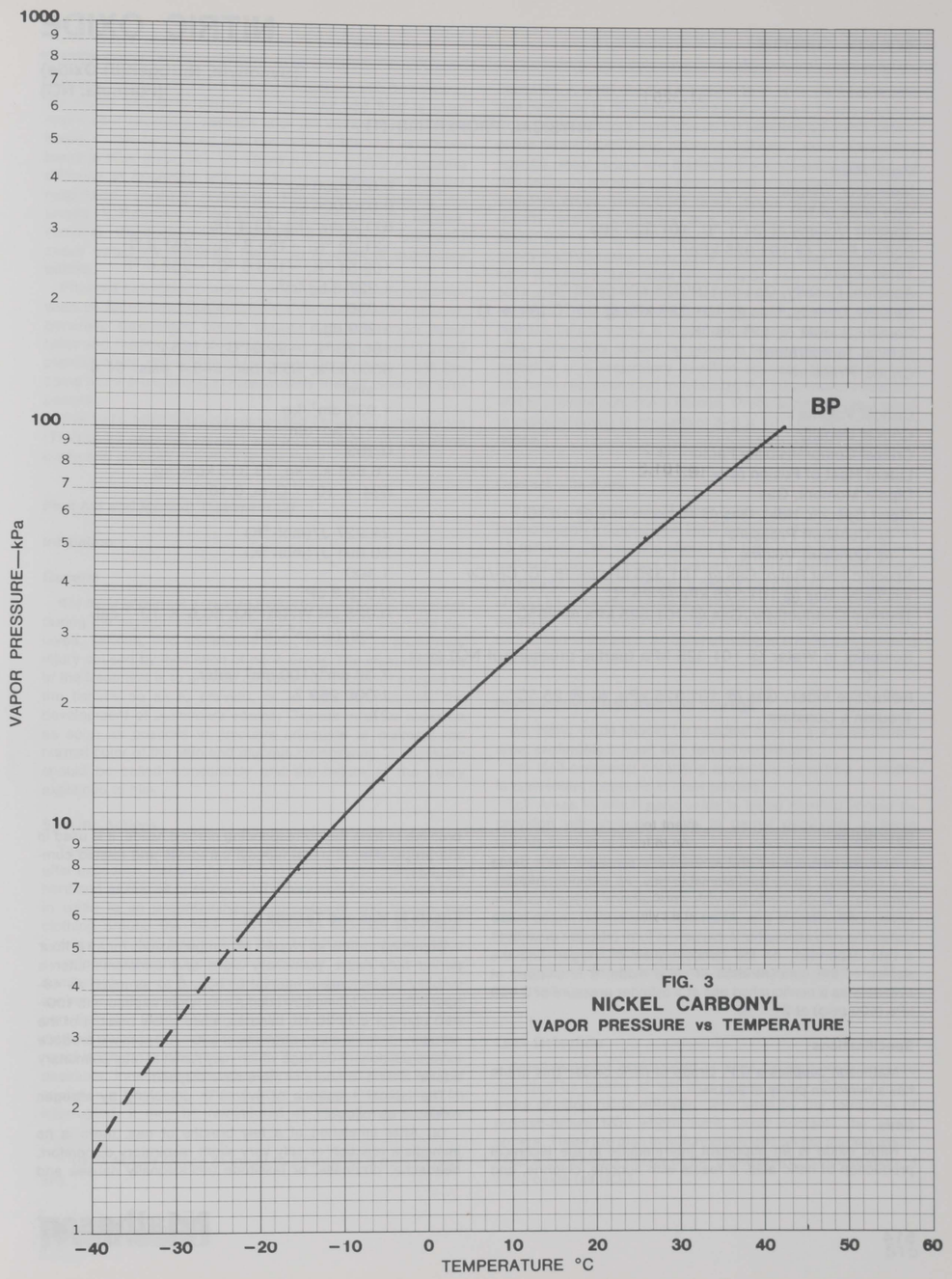


FIG. 3
NICKEL CARBONYL
VAPOR PRESSURE vs TEMPERATURE

NITRIC OXIDE

(Synonym: Nitrogen(II) Oxide)
(Formula: NO)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.030 006 kg
One Mole of NO	0.030 006 kg
Specific Volume @ 21.1 °C, 101.325 kPa	811.6 dm^3/kg; 13 ft^3/lb
Boiling Point @ 101.325 kPa	121.38 °K; −151.8 °C; −241.2 °F
Triple Point	109.51 °K; −163.6 °C; −262.6 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	1.227 8 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.036
Density, Liquid @ 121.38 °K	1.269 kg/l
Critical Temperature	180.25 °K; −92.9 °C; −135.2 °F
Critical Pressure	6550 kPa; 65.5 bar; 949.4 psia; 64.6 atm
Critical Volume	1.933 dm^3/kg
Critical Density	0.517 kg/dm^3
Critical Compressibility Factor	0.253
Latent Heat of Fusion @ −163.6 °C	76.621 kJ/kg; 18.313 kcal/kg
Dipole Moment, Gas	534×10^{-33} C·m; 0.16 D
Molar Specific Heat, Gas @ 101.325 kPa @ 15 °C	
@ Constant Pressure	29.227 J/(mol·°K)
@ Constant Volume	20.891 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 15 °C, Cp/Cv	1.400
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.018 8 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25°C	0.025 36 W/(m·°K); 60.6×10^{-6} cal·cm/(s·cm^2·°C)
Solubility In Water @ 101.325 kPa (partial pressure of NO) @ 0 °C	7.38 cm^3/100 cm^3 water
Refractive Index, Gas @ 101.325 kPa, n_D @ 25 °C	1.000 269 7
Trouton's Constant	27.1

Description

At room temperature and atmospheric pressure, nitric oxide is a colorless, toxic, nonflammable gas. At ambient temperature, nitric oxide combines with atmospheric oxygen to form toxic, nonflammable gas. At ambient temperature, nitric oxide combines with atmospheric oxygen to form nitrogen dioxide at a rate dependent on the concentration of oxygen and the square of the concentration of nitric oxide. It is shipped in cylinders as a nonliquefied gas at a cylinder pressure of 3 450 kPa (500 psig) at 21.1 °C.

Specifications

Matheson supplies a C.P. Grade of nitric oxide. This grade has a minimum purity of 99.0%.

Uses

Nitric oxide is an important intermediate in the technical production of nitric acid. It reacts with fluorine, chlorine, and bromine to form the corresponding nitrosyl halide. It is used in the preparation of metal nitrosyl carbonyls and related compounds.

Effects In Man and Toxicity (2)

Breathing as little as 25 ppm of nitrogen oxides for an 8-hour period may cause pulmonary signs and symptoms after a virtually asymptomatic interval of from 5 to as much as 48-hours. Delayed pulmonary edema may follow exposure to 100-150 ppm for only 30-60 minutes, while a few breaths of the nitrogen oxides in concentrations of 200-700 ppm will produce severe pulmonary damage which may result in fatal pulmonary edema after 5-8 hours or more have elapsed.

The typical sequence of events in poisoning by nitrogen oxides is as follows:

(a) After inhalation of a few breaths of gas, there is no immediate reaction or only very slight respiratory discomfort, headache, dizziness, or lassitude (occasionally nausea and

vomiting may appear which usually disappears with 30 minutes; the victim frequently persists in his work. (b) Five to eight hours after exposure, perhaps after the worker has returned home, it may be noticed that the victim's lips and ears have become blue (cyanotic); (c) There follows rapidly increasing difficulty in breathing with accelerated, somewhat irregular respiration, choking, dizziness, headache, increasing cyanosis, a tightness in the chest; and occasionally nausea, vomiting, lassitude, and palpitation also occurs. Untreated cases frequently terminate fatally as a result of pulmonary edema.

Physical examination within a short time after exposure reveals an accelerated respiratory rate, decreased vital capacity, generally suppressed breath sounds with occasional moist rates and rhonchi, low blood pressure, and an elevated blood platelet count (10-100% above normal); all these signs become more pronounced in inadequately treated cases as time passes.

The 1979 ACGIH has recommended Threshold Limit Values (TLV) of 25 ppm (30 mg/m^3) and 5 ppm (9 mg/m^3) for nitric oxide and nitrogen dioxide,* respectively.

First Aid and Medical Treatment (2)

Inhalation

General

It is most important to realize that prompt, efficient treatment during the asymptomatic period may completely avert the delayed, serious, and sometimes fatal, sequelae of pulmonary injury caused by inhalation of nitric oxide. The main objective of the treatment is to provide an adequate supply of oxygen to the tissues so as to prevent, or at least to minimize, the development of pulmonary edema. Oxygen must be supplied as soon as possible in amounts adequate to maintain the normal color of the skin and mucous membranes. A physician should be called immediately and the nature of the injury explained to him.

Specific Actions

Terminate the exposure immediately. If encountered shortly after exposure, instruct the victim to breathe maximally, i.e., as hard and as fast as possible. Carry the victim (do not allow him to walk) to an uncontaminated atmosphere and loosen the clothing around the neck and chest to facilitate breathing. Enforce complete bed rest for 24 to 48 hours, whether toxic symptoms and signs are recognized or not, and keep the victim comfortably warm. As soon as there is any indication of poisoning (coughing, difficulty in breathing, or fatigue), start oxygen therapy. Pure oxygen should be administered by any method which insures high inspiratory concentrations. An oronasal mask is usually best. A slightly positive gas pressure is desirable. Inhalation of oxygen should not exceed 1 hour of continuous treatment. After 1 hour oxygen therapy may be interrupted. It may be reinstituted as the clinical condition indicates. A small dose of morphine (e.g., 1×10^{-6} kg) is safe and desirable to diminish anxiety and dyspnea. Frothy exudate from the respiratory tract should be removed by some appropriate means (suctioning, postural drainage, use of antifoaming agents). Most drugs are ineffective and possibly harmful; in this category are atropine, epinephrine, expectorants, emetics, sedative drugs (except for small doses of morphine), and usually cardiac glycosides. In a few instances, rapid digitalization with a drug like ouabain may be advisable. An emergency tracheostomy under local anesthesia may make it possible to remove foam more effectively by a suctioning catheter, but it usually complicates the administration of oxygen. Artificial respiration may become necessary, but unless airway obstruction can be corrected, it is seldom effective. Penicillin and/or other antibiotics should be given in large doses as soon as evidence of a respiratory infection appears. Steroid therapy has been recommended to minimize the inflammatory reaction and to prevent pulmonary fibrosis. Prednisone has been given to exposed adults in amounts of $3-8 \times 10^{-6}$ kg daily in divided doses.

* 1979 ACGIH Notice of Intent to change to 3 ppm (6 mg/m^3).

Contact with Eyes

If high concentrations of vapor contact the eyes, they should be thoroughly irrigated with large amounts of water for at least 15 minutes. The eyelids should be held apart during the irrigation to insure contact of water with all of the tissues of the surface of the eyes and lids. If pain is still present, the irrigation should be continued for an additional 15 minutes. As a first aid measure, 2 or 3 drops of a 0.5% pontocaine solution may then be instilled in the eyes. An ophthalmologist should be consulted at once.

Precautions in Handling and Storage

(a) Nitric oxide should be handled only in a well-ventilated area, preferably a hood with forced ventilation.

(b) Self-contained breathing apparatus should be available in convenient locations in emergencies.

(c) Areas in which nitric oxide is being handled should be provided with enough exists to permit personnel to leave quickly in case of trouble.

(d) Personnel should have available for immediate use NIOSH-approved gas masks for emergencies.

(e) Air contamination should be avoided in high pressure reactions of nitric oxide with organic compounds. Air contamination would lead to the formation of nitrogen dioxide which could cause an ignition or detonation.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Small leaks of nitric oxide in lines or equipment may be detected by means of wet blue litmus paper. Sites of large leaks of nitric oxide are also detectable by the formation of reddish-brown NO_2 where nitric oxide contacts the atmosphere. There are also monitoring devices on the market which keep a continuous check of the atmospheric concentration of nitric oxide (as NO_2).

Analytical Detection (3)

A method is described by Kain, *et al.*, for the determination of nitric oxide with moist starch-iodide paper after oxidation by oxygen in air. The practical threshold of sensitivity of starch-iodide paper for nitric oxide, when a 5-ml. sample of test gas is mixed with 15 ml of oxygen, is 300 ppm for a color change within 5 minutes. It appears to be better than litmus for this purpose.

The same authors describe a more sensitive (10-100 ppm) method of detection of nitric oxide. This method employs test kits having silica gel columns with a reactive reagent. The method depends on a color reaction, with the length of color change along the column giving an indication of the approximate concentration of nitrogen dioxide in the standard volume of gas tested, the nitric oxide first being oxidized ($KMnO_4$) to nitrogen dioxide.

Finally, Kain, *et al.*, describe the most sensitive (1 ppm) method for the determination of nitric oxide, involving oxidation to nitrogen dioxide, dissolution in water, diazotization of sulfanilic acid with the nitrous acid present, coupling with N-(1-naphthyl)ethylenediamine, followed spectrophotometric measurement of the intensity of the color developed.

Disposal of Leaking Cylinders

Leaking cylinders of nitric oxide may be disposed of as follows:

Transfer cylinder to a hood or safe out-of-doors location, after donning appropriate breathing apparatus. Attach appropriate regulator with long piece of flexible hose. Introduce the gas into an adequate amount of alkaline potassium permanganate solution. The reaction is: $NO + KMnO_4 \rightarrow KNO_3 + MnO_2$.

Alternatively, the nitric oxide may be converted with excess air in a mixing device into a mixture of nitric oxide and nitrogen dioxide and the resulting mixture introduced into caustic solution, a mixture of sodium nitrate and nitrite resulting.

Materials of Construction

Since nitric oxide is noncorrosive, most common metals of construction can be used. However, in the presence of oxygen and moisture, corrosive conditions will develop due to the formation of nitric and nitrous acids. Therefore, prior to use, systems to contain nitric oxide should be purged with an inert gas. Where air contamination cannot be eliminated, 18-8 stainless steel should be used.

Cylinder and Valve Description

Nitric oxide is shipped in DOT approved, high pressure, steel cylinders. Cylinders of nitric oxide are equipped with stainless steel valves having Compressed Gas Association (CGA) approved alternate cylinder valve outlet No. 660. The valve outlet has a thread size of 1.030 inches with right-hand external threads with a flat seat and using a washer as a seal (see Figure 1 for an illustration of this valve outlet and its mating connection). Lecture bottles have a special 5/16 inch 32 threads per inch, female outlet.

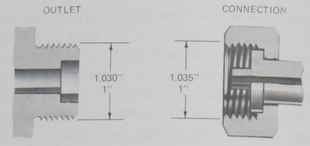


Fig. 1 CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

Safety Devices

No safety devices are permitted to be used on cylinders of nitric oxide.

Recommended Controls

Automatic Pressure Regulators

Matheson supplies single stage regulator Model 14-660 for nitric oxide service. The regulator has an anodized aluminum body, a diaphragm of FEP Teflon on Neoprene, a seat of Teflon, and internal parts of type 316 stainless steel. The regulator is provided with two gauges, one for cylinder pressure and one for delivery pressure; its delivery pressure is 28-550 kPa (4-80 psig). To prevent suckback of foreign materials into the regulator a stainless steel check valve should be used.

Two stage regulator Model 3800-660 is also available for nitric oxide service. This regulator has a body and diaphragm of type 316 stainless steel, Kel-F seat and Kel-F and Teflon gaskets. It is provided with a diaphragm packless outlet valve with a 1/4" Gyrolok tube fitting. It has a delivery pressure range of 28-620 kPa (4-90 psig).

Manual Controls

For manual flow control, Matheson has available needle valve Model 61A-660, of stainless steel, for direct attachment to the cylinder valve outlet. This valve is supplied with a 1/4" tube fitting outlet connection. It should be used only where manual control is required since it will not prevent pressure from building up if the system becomes clogged or if the system itself is closed. A Model 59 needle valve is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8340 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Nitric oxide is classified as a "Class A" poison gas by the DOT and is shipped under a "Poison Gas Label".

Chemical Preparation

Nitric oxide is formed when acid solutions of nitrates or nitrites are reduced by metals.

$$8HNO_3 + 3Cu \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$

$$2KNO_2 + 6Hg + 4H_2SO_4 \rightarrow 2NO + 3Hg_2SO_4 + K_2SO_4 + 4H_2O$$

or other reducing agents

$$2KNO_3 + 4H_2SO_4 + 6FeSO_4 \rightarrow 3Fe_2(SO_4)_3 + 2NO + K_2SO_4 + 4H_2O$$

$$2HI + 2HNO_2 \rightarrow I_2 + 2NO + 2H_2O.$$

The large-scale preparation of NO involves the oxidation of ammonia above 500 °C in the presence of platinum

$$4NH_3 + 5O_2 \rightarrow 4\ NO + 6H_2O.$$

Direct combination of the elements occurs under energy-rich conditions

$$N_2 + O_2 \rightleftarrows 2\ NO,$$

but the equilibrium is unfavorable even at high temperatures, about 5 volume % of NO being formed at 3 200 °C.

Chemical Properties (4)

Nitric oxide is thermodynamically unstable at room temperature, the liquid or compressed gas slowly undergoing disproportionation:

$$4NO \rightarrow N_2O_3 + N_2O,$$

In the gaseous state it is colorless and shows no tendency to dimerize. In the liquid and solid states, nitric oxide is blue and dimerizes. At elevated temperatures, nitric oxide is an oxidizing agent and will support the combustion of materials such as phosphorous. It is reactive to oxidizing agents, being converted to nitric acid by permanganate, to NO_2 by oxygen, and to nitrosyl halides by fluorine, chlorine, and bromine. Nitric oxide gives complexes with a number of metal ions and adds to certain metals and metal carbonyls.

At ambient temperature nitric oxide combines with molecular oxygen to form nitrogen dioxide at a rate which is dependent on the concentration of oxygen and the square of the concentration of nitric oxide. At very low concentrations, the oxidation is slow, e.g., at 10 ppm 7 hours are required for 50% oxidation. At 10 000 ppm, however, 50% oxidation is achieved in about 24 seconds.

Thermodynamic and Detailed Physical Data

Molecular Structure

The heteropolar nitric oxide molecule has $C_{\infty v}$ symmetry and a symmetry number of one, with a N—O bond distance of 1.150 8 Å ($1.150\ 8 \times 10^{-10}$ m). The nitric oxide molecule contains an odd number of electrons, but it is rather inactive chemically in comparison with other odd molecules. The observed bond distance of $1.150\ 8 \times 10^{-10}$ m (1.150 8 Å) lies between that estimated for double and triple bonds, namely 1.18×10^{-10} m (1.18 Å) and 1.06×10^{-10} m (1.06 Å), respectively.

Two electronic structures are suggested :N::O: or :N⋮⋮O:. This arrangement stabilizes the molecule sufficiently with respect to the structure :N::O: so that some unusual properties result.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous nitric oxide.

Vapor Pressure (5)

The vapor pressure of liquid nitric oxide from 100 [mmHg] to 1 500 mmHg is represented by the following Antoine vapor pressure equation:

$$\log_{10}p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10}p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 8.743 00, 682.938, and 268.27, respectively.

Temperature, °K	Vapor Pressure		
	kPa	mbar	mmHg
106.16	13.332	133.2	100
110.89	26.664	266.6	200
113.87	39.997	400.0	300
116.09	53.329	533.3	400
117.87	66.661	666.6	500
119.37	79.993	799.9	600
120.67	93.325	933.3	700
121.38	101.325	1 013.25	760
121.82	106.658	1 067	800
122.86	119.990	1 200	900
123.80	133.322	1 333	1 000
125.46	159.986	1 600	1 200
127.56	199.983	2 000	1 500

Latent Heat of Vaporization @ 121.41 °K	13.776 2 kJ/mol; 3.292 6 kcal/mol

Thermodynamic Data

Thermodynamic properties of superheated nitric oxide are shown in Table 1. Compressibility data appear in Table 2.

Thermodynamic Properties of Nitric Oxide As Ideal Gas @ 25 °C (6)

Heat Capacity, C_p°	29.844 J/(mol·°K)
Entropy, S°	210.652 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−210.652 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	9.192 kJ/(mol)
Enthalpy of Formation, ΔH_f°	90.291 kJ/mol
Free Energy of Formation, ΔF_f°	86.596 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of nitric oxide, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 110-115, Matheson, Lyndhurst, New Jersey.

[3] M. L. Kain, *et al.*, *Brit. J. Anaesthesia*, 39, 425-431 (1967).

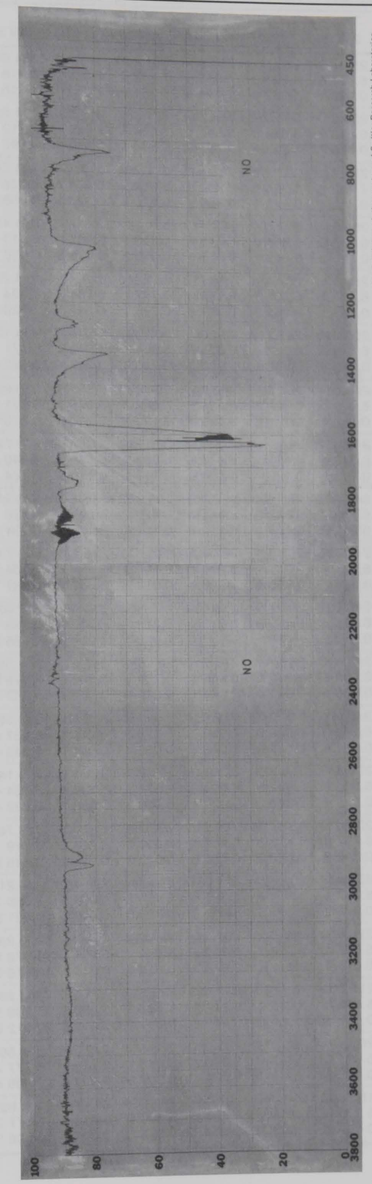
[4] C. Prys-Roberts, *Brit. J. Anaesthesia*, 39, 432-439 (1967).

[5] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds*, *1968*, Volume 1, Thermodynamic Research Center, Texas A & M University, College Station, Texas.

[6] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U.S. Government Printing Office, Washington, D.C.

[7] *The Sadtler Standard Spectra*, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[8] J. Opfell, W. G. Schlinger, and B. H. Sage, *Ind. Eng. Chem.* 46, 189 (1954).



Reprinted through the courtesy of Sadtler Research Laboratories
© Sadtler 1972

Fig. 2. Infrared spectrum of gaseous nitric oxide over the frequency range of 3 800 cm^{-1} to 450 cm^{-1}; 10 cm path length cell, with KBr optics; cell pressure 0.533 kPa (4 mmHg) (7).

Table 1. THERMODYNAMIC PROPERTIES OF SUPERHEATED NITRIC OXIDE (8)

H, ENTHALPY, kJ/kg; **S**, ENTROPY, kJ/(kg·°K); **V**, SPECIFIC VOLUME, m^3/kg

Pressure kPa	Pressure atm		Temperature, °K 210.93	227.59	244.26	260.87	277.59	294.26	310.93	327.59	344.26	360.93	377.59
68.948	0.680	H	217.824	234.699	251.482	268.194	284.837	301.480	318.077	334.697	351.293	367.903	384.510
		S	6.776 8	6.853 8	6.925 8	6.991 0	7.053 0	7.112 0	7.165 9	7.218 7	7.268 4	7.314 9	7.358 0
		V	0.845 9	0.913 3	0.980 1	1.047 5	1.114 3	1.181 8	1.249.2	1.316 0	1.383 4	1.387 8	1.517 0
101.325	1.00	H	217.638	234.536	251.342	268.055	284.744	301.387	318.007	334.627	351.247	367.843	384.440
		S	6.669 7	6.746 7	6.818 2	6.884 8	6.947 1	7.004 9	7.059 7	7.112 4	7.160 9	7.206 9	7.250 5
		V	0.575 0	0.621 2	0.666 7	0.712 3	0.757 9	0.804 1	0.849 6	0.895 2	0.940 8	0.986 4	1.031 9
137.895	1.36	H	217.405	234.350	251.179	267.939	284.628	301.294	317.937	334.557	351.177	367.797	384.393
		S	6.583 5	6.660 9	7.732 5	6.798 6	6.860 9	6.919 9	6.974 7	7.026 6	7.075 6	7.121 6	7.165 9
		V	0.422 0	0.455 7	0.489 4	0.523 1	0.556 9	0.590 6	0.624 3	0.658 0	0.691 1	0.724 8	0.758 5
206.843	2.04	H	216.964	234.025	250.900	267.683	284.419	301.132	317.798	334.418	351.061	367.681	384.277
		S	6.469 7	6.548 0	6.619 5	6.686 0	6.748 4	6.806 5	6.862 2	6.913 6	6.962 6	7.009 0	7.053 0
		V	0.280 9	0.303 4	0.325 9	0.348 3	0.370 8	0.393 3	0.415 8	0.438 2	0.460 7	0.483 2	0.505 7
275.790	2.72	H	216.545	233.676	250.598	267.451	284.210	300.946	317.403	334.278	350.945	367.564	384.184
		S	6.389 0	6.466 8	6.538 8	6.605 7	6.668 0	6.727 0	6.781 8	6.834 1	6.883 1	6.929 5	6.973 1
		V	0.210 4	0.227 2	0.244 1	0.260 9	0.277 8	0.295 3	0.312 1	0.328 4	0.345 2	0.362 1	0.378 9
344.738	3.40	H	216.127	233.330	250.319	267.218	284.001	300.597	317.356	334.139	350.805	367.448	384.084
		S	6.325 4	6.404 0	6.476 4	6.543 4	6.605.7	6.664 7	6.719 9	6.771 8	6.820 8	6.867 2	6.911 6
		V	0.167 7	0.181 6	0.195 4	0.208 5	0.222 2	0.236 0	0.249 1	0.262 8	0.276 6	0.289 7	0.302 8
413.685	4.08	H	215.708	232.979	250.017	266.962	283.791	300.365	317.310	333.999	350.689	367.332	383.998
		S	6.273 5	6.352 6	6.425 0	6.492 3	6.554 7	6.613 6	6.668 9	6.721 2	6.770 1	6.816 6	6.860 5
		V	0.139 5	0.151 1	0.162 4	0.173 8	0.185 1	0.196 6	0.207 9	0.219 1	0.230 4	0.241 6	0.252 8
551.581	5.44	H	214.848	232.258	249.436	266.474	283.373	300.202	316.984	333.720	350.433	367.123	383.789
		S	6.191 1	6.270 6	6.343 4	6.411 1	6.473 9	6.532 9	6.588 5	6.640 8	6.689 8	6.736 2	6.780 6
		V	0.104 3	0.112 9	0.121 5	0.130 1	0.138 6	0.147 1	0.155 6	0.164 1	0.172 5	0.180 9	0.189 2
689.476	6.80	H	214.012	231.561	248.855	265.963	282.955	299.807	316.659	333.441	350.177	366.890	383.603
		S	6.126 2	6.206 5	6.280 2	6.348 0	6.411 1	6.470 1	6.525 8	6.578 5	6.627 5	6.674 3	6.718 2
		V	0.083 0	0.090 1	0.097 0	0.103 9	0.110 7	0.117 6	0.124 4	0.131 2	0.137 9	0.144 6	0.151 4
1 034.214	10.21	H	211.850	229.795	247.391	264.731	281.885	298.923	315.869	332.744	349.550	366.332	383.092
		S	6.006 6	6.088 6	6.163 4	6.232 1	6.296 1	6.355 9	6.411 6	6.464 3	6.514 1	6.560 5	6.604 9
		V	0.054 8	0.059 6	0.064 3	0.068 9	0.073 5	0.078 2	0.082 7	0.087 3	0.091 8	0.096 3	0.100 8
1 378.951	13.61	H	209.642	228.005	245.903	263.476	280.839	297.994	315.032	332.024	348.922	365.798	382.603
		S	5.919 5	6.003 2	6.079 4	6.148 8	6.213 7	6.273 9	6.330 0	6.383 1	6.432 9	6.479 8	6.524 5
		V	0.040 6	0.044 3	0.047 9	—	—	0.058 4	0.061 9	0.065 3	0.068 7	0.072 2	0.075 5
1 723.689	17.01	H	207.410	226.192	244.415	262.221	279.747	297.064	314.218	331.303	348.295	365.240	382.115
		S	5.849 7	5.935 4	6.012 8	6.083 5	6.148 8	6.209 5	6.266 4	6.319 5	6.369 7	6.417 0	6.461 4
		V	0.032 2	0.035 2	0.038 1	0.041 0	0.044 1	0.046 6	0.049 4	0.052 2	0.054 9	0.057 7	0.060 4
2 068.427	20.41	H	205.155	224.355	242.904	260.942	278.654	296.134	313.405	330.582	347.644	364.659	381.604
		S	5.791 5	5.878 9	5.958 0	6.029 6	6.095 7	6.156 8	6.214 1	6.267 6	6.317 8	6.365 1	6.409 9
		V	0.026 5	0.029 1	0.031 6	0.034 0	0.036 4	0.038 7	0.041 1	0.043 4	0.045 7	0.048 0	0.050 3
2 757.903	27.22	H	200.530	220.636	239.813	258.362	276.446	294.228	311.778	329.141	346.389	363.543	380.604
		S	5.695 7	5.787 3	5.868 9	5.942 5	6.009 9	6.072 2	6.130 4	6.184 4	6.235 4	6.283 1	6.328 3
		V	0.019 4	0.021 4	0.023 4	0.025 2	0.027 1	0.028 9	0.030 7	0.032 4	0.034 2	0.035 9	0.037 6
3 447.378	34.02	H	195.765	216.801	236.675	255.712	274.215	292.299	310.104	327.700	345.110	362.427	379.605
		S	5.617 0	5.713 3	5.797 8	5.873 1	5.942 1	6.005 3	6.064 3	6.119 1	6.170 6	6.218 7	6.264 3
		V	0.015 2	0.016 8	0.018 5	0.020 0	0.021 5	0.023 0	0.024 4	0.025 9	0.027 3	0.028 7	0.030 1
4 136.854	40.83	H	190.814	212.873	233.467	253.039	271.937	290.346	308.407	326.212	343.832	361.265	378.605
		S	5.549 2	5.649 7	5.737 5	5.814 9	5.885 6	5.950 1	6.009 5	6.065 1	6.117 0	6.166 0	6.211 6
		V	0.012 3	0.013 8	0.015 2	0.016 5	0.017 8	0.019 0	0.020 3	0.021 5	0.022 7	0.023 9	0.025 0
5 515.806	54.44	H	180.377	204.691	226.819	247.530	267.311	286.395	304.990	323.237	341.228	358.987	378.583
		S	5.432 1	5.543 0	5.637 1	5.719 5	5.793 2	5.859 7	5.921 1	5.978 5	6.031 7	6.081 0	6.127 5
		V	0.008 71	0.009 95	0.011 1	0.012 1	0.013 2	0.014 1	0.015 1	0.016 0	0.016 9	0.017 8	0.018 7
6 894.757	68.05	H	169.057	196.020	219.892	241.835	262.523	282.327	301.527	302.239	338.602	356.686	374.538
		S	5.329 2	5.452 2	5.553 8	5.640 9	5.717 9	5.787 3	5.850 9	5.909 1	5.963 5	6.013 7	6.060 9
		V	0.006 53	0.007 64	0.008 62	0.009 53	0.010 4	0.011 2	0.012 0	0.012 8	0.013 5	0.014 3	0.015 0
10 342.136	102.1	H	135.957	171.893	201.181	226.750	250.040	271.844	292.578	312.568	331.954	350.921	369.517
		S	5.093 2	5.257 6	5.381 9	5.483 6	5.570 2	5.688 1	5.714 9	5.777 7	5.834 6	5.887 7	5.936 7
		V	0.003 54	0.004 53	0.005 34	0.006 05	0.006 70	0.007 30	0.007 88	0.008 43	0.008 97	0.009 49	0.010 0
13 789.514	136.1	H	103.019	145.138	180.865	210.850	237.047	261.035	283.489	304.828	325.329	345.203	364.566
		S	4.891 9	5.084 0	5.235 9	5.355 1	5.452 6	5.536 7	5.610 7	5.677 3	5.737 9	5.793 6	5.844 6
		V	0.002 20	0.003 01	0.003 73	0.004 35	0.004 89	0.005 39	0.005 87	0.006 31	0.006 74	0.007 15	0.007 55

Table 2. COMPRESSIBILITY FACTORS FOR NITRIC OXIDE

Pressure kPa	Temperature, °K 266.48	272.04	277.59	283.15	288.71	294.26	299.82	305.37	310.93	316.48	322.04
137.895	0.998 0	0.998 1	0.998 3	0.998 4	0.998 2	0.998 3	0.998 5	0.998 6	0.998 7	0.998 8	0.998 9
275.790	0.996 0	0.996 3	0.996 5	0.996 8	0.996 4	0.996 7	0.996 9	0.997 2	0.997 4	0.997 6	0.997 8
413.685	0.994 0	0.994 4	0.994 8	0.995 1	0.994 6	0.995 0	0.995 4	0.995 8	0.996 1	0.996 4	0.996 7
689.476	0.989 9	0.990 6	0.991 3	0.991 9	0.991 1	0.991 8	0.992 4	0.993 0	0.993 5	0.994 0	0.994 5
1 378.95	0.979 8	0.981 3	0.982 5	0.983 8	0.982 5	0.983 9	0.985 1	0.986 2	0.987 3	0.988 2	0.989 1
2 757.90	0.959 6	0.962 5	0.965 1	0.967 6	0.966 2	0.968 8	0.971 2	0.973 4	0.975 4	0.977 3	0.979 0
4 136 85	0.939 5	0.943 9	0.947 8	0.951 8	0.951 1	0.954 8	0.958 3	0.961 4	0.964 4	0.967 1	0.969 6
5 515.81	0.919 6	0.925 6	0.930 9	0.936 2	0.937 1	0.941 8	0.946 3	0.950 4	0.954 2	0.957 7	0.960 9
6 894.76	0.900 1	0.907 8	0.914 5	0.921 1	0.924 1	0.929 9	0.935 2	0.940 2	0.944 7	0.949 0	0.952 9
8 273.71	0.881 2	0.890 5	0.898 6	0.906 6	0.912 2	0.918 9	0.925 1	0.930 8	0.936 1	0.941 0	0.945 6
11 031.6	0.845 7	0.858 2	0.869 0	0.879 8	0.891 5	0.899 7	0.907 3	0.914 4	0.921 0	0.927 2	0.932 9
13 789.5	0.814 2	0.830 0	0.843 4	0.856 8	0.874 7	0.884 1	0.892 9	0.901 1	0.908 8	0.916 0	0.922 7
17 236.9	0.782 5	0.802 0	0.818 3	0.834 5	0.858 7	0.869 3	0.879 2	0.888 6	0.897 4	0.905 6	0.913 3
20 684.3	0.795 9	0.809 8	0.823 1	0.835 8	0.847 9	0.859 3	0.870 1	0.880 2	0.889 8	0.898 8	0.907 3

NITROGEN

(Formula: N_2)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.028 013 4 kg
One Mole of N_2	0.028 013 4 kg
Specific Volume @ 21.1 °C, 101.325 kPa	861.5 dm^3/kg; 13.8 ft^3/lb
Boiling Point @ 101.325 kPa	77.352 °K; −195.8 °C; −320.4 °F
Triple Point	
Temperature	63.149 °K; −210.0 °C; −346.0 °F
Pressure	12.53 kPa; 125.3 mbar; 94.01 mmHg
Absolute Density, Gas @ 101.325 kPa @ 25 °C	1.145 5 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C	0.967
Density, Liquid @ Saturation Pressure @ 63.15 °K	0.808 kg/l
Critical Temperature	126.26 °K; −146.9 °C; −232.4 °F
Critical Pressure	3 400 kPa; 34.0 bar; 492.9 psia; 33.54 atm
Critical Volume	3.216 dm^3/kg
Critical Density	0.311 kg/dm^3
Critical Compressibility Factor	0.291 6
Latent Heat of Fusion @ 63.19 °K	7 209.03 J/mol; 1 723.0 cal/mol
Dipole Moment, Gas	0 C·m
Molar Specific Heat, Gas @ 101.325 kPa @ 26.8 °C	
@ Constant Pressure	28.98 J/(mol·°K)
@ Constant Volume	20.6 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.326 kPa 16.8 °C, Cp/Cv	1.407
Molar Specific Heat, Liquid @ Saturation Pressure @ 100 °K	64.0 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 26.8 °C	0.017 87 mPa·s; 0.017 87 cP
Viscosity, Liquid @ Saturation Pressure @ 63.9 °K	0.292 mPa·s; 0.292 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 26.8 °C	0.025 9 W/(m·°K); 61.9 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ Saturation Pressure @ 65 °K	0.159 8 W/(m·°K); 381.9 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 70.15 K	10.5 mN/m; 10.5 dyn/cm
Solubility In Water @ 101.325 kPa (partial pressure of Nitrogen) @ 25 °C	1.485 cm^3/100 cm^3 water
Refractive Index, Gas @ 101.325 kPa, n_D @ 25 °C	1.000 273 2
Dielectric Constant, Gas @ 101.325 kPa @ 20 °C	1.000 548 0
Dielectric Constant, Liquid @ 70.15 °K	1.454
Velocity of Sound In Nitrogen @ 101.325 kPa @ 0 °C	336.96 m/s

Diffusivities of Nitrogen In Other Gases @ 101.325 kPa:

Other Gas	Temperature, °C	Diffusivity, cm^2/s
Argon	20	0.194
Carbon dioxide	20	0.163
Helium	20	0.705
Hydrogen	0	0.674
Oxygen	0	0.181

Description

At room temperature and atmospheric pressure, nitrogen is a colorless, odorless, nontoxic, nonflammable gas. It constitutes 78% by volume of the atmosphere. Naturally occurring nitrogen contains two isotopes, ^{14}N and ^{15}N, with a relative abundance of 99.62% and 0.38%, respectively (1). Gaseous nitrogen is shipped in cylinders and tube trailers. Liquid nitrogen is shipped in specially authorized cylinders, in heavily insulated portable containers, and, in bulk, in tank trucks and truck trailers. Nitrogen is normally available in cylinders compressed to 17 170 kPa (2 490 psig) and 13 790 kPa (2 000 psig) at 21.1 °C.

Specifications

Matheson supplies nine grades of nitrogen, the specifications of which are as follows:

1. Research Purity Grade

This grade of nitrogen has a minimum purity of 99.999 5 mole %. It is supplied in small cylinders and glass flasks.

2. Matheson Purity Grade

This grade has a minimum purity of 99.999 5 mole %.

3. NO_x Free Grade

This grade of nitrogen contains a maximum of 10 parts per billion of NO_x.

4. Ultra High Purity Grade

This grade of nitrogen has a minimum purity of 99.999 mole %.

5. Zero Gas Grade

This grade of nitrogen contains less than 0.5 ppm total hydrocarbons as methane.

6. Oxygen Free Grade

This grade of nitrogen contains less than 5 ppm oxygen.

7. Prepurified Grade

This grade of nitrogen has a minimum purity of 99.998%.

8. High Purity Grade

This grade of nitrogen has a minimum purity of 99.99%.

9. Extra Dry Grade

This grade of nitrogen has a minimum purity of 99.9%.

Uses

Nitrogen is used as an inert gas in electrical systems, the chemical industry, and in the food packaging industry. Nitrogen also finds extensive use as an inert atmosphere, and in the filling of some incandescent lamps.

Toxicity

Nitrogen is nontoxic but can act as an asphyxiant by displacing the necessary amount of air to sustain life.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Leak Detection

Leaks in lines and equipment may be detected by painting the suspected sites with soapy water. Leaks will be evident by bubble formation.

Disposal of Leaking Cylinders

For disposal see Appendix II-C.

Materials of Construction

Since nitrogen is inert no special materials of construction are required. However, any piping or vessels containing nitrogen should be designed to have a working pressure as specified by competent engineers, using a safety factor conforming to the A.S.M.E. code for pressure piping.

Cylinder and Valve Description

Nitrogen is packaged in DOT approved, high pressure steel cylinders. Matheson employs Compressed Gas Association (CGA) valve outlet connection No. 580 on all cylinders of nitrogen except those at 41 370 kPa (6 000 psig). This standard cylinder valve outlet has a diameter of 0.965 inch and right-hand internal threads, accepting a bullet-shaped nipple (see Figure 1 for this valve outlet and its mating connection). Cylinders at 41 370 kPa (6 000 psig) are equipped with CGA valve outlet connection No. 677 (see Figure 2). Lecture bottles have special 5/16"-32 threads per inch, female valve outlets and a 5/16"-18 threads per inch, male dual valve outlet.

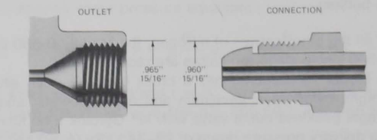


Fig. 1. CONNECTION 580 .965"-14 RH INT. accepting a Bullet Shaped Nipple

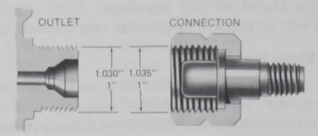


Fig. 2. CONNECTION 677 1.030"-14 LH EXT. accepting Round Shaped Nipple

Safety Devices

Cylinders containing nitrogen have safety devices of either the frangible disc type or frangible disc type backed up with fusible metal, melting at approximately 100 °C (212 °F). Cylinders pressurized 10% of excess of their marked service pressure in accordance with present DOT regulations must be equipped only with safety devices of the unbacked frangible disc type. These safety devices are usually an integral part of the cylinder valve, situated opposite the valve outlet.

Recommended Controls

In order to reduce the high cylinder pressure of nitrogen to a safe working value consistent with a system's design, the following types of controls are recommended.

Automatic Pressure Regulators

1. Single Stage Automatic Regulators

A single stage regulator will reduce cylinder pressure to a delivery pressure in a particular range, depending upon the design of the regulator and its spring load. A single stage regulator will show a slight variation in delivery pressure as cylinder pressure falls. The following single stage regulators are available from Matheson for use with Prepurified, High Purity, and Extra Dry Grades of nitrogen.

Model No.	Delivery Pressure Range kPa	bar (g)	psig
1L-580	28–550	0.28–5.5	4–80
1H-580	69–1 240	0.69–12.4	10–180
2-580	345–4 480	3.45–44.8	50–650
3-580	690–10 340	6.9–103.4	100–1 500
4-580	690–17 240	6.9–172.4	100–2 500
3320 (for lecture bottles)	28–410	0.28–4.1	4–60

For all the other grades of nitrogen, the Model 19-580 and 3500-580 single stage regulators are recommended.

The Model 19 regulator has a brass body, German silver diaphragm, nylon seat, aluminum and nylon gaskets, and a diaphragm packless outlet valve with ¼" Gyrolok tube fitting. It has a delivery pressure range of 28–345 kPa (4–50 psig).

The Model 3500 regulator has a type 316 stainless steel body, a Teflon-lined type 301 stainless steel diaphragm, Kel-F seat, Teflon gaskets, and a diaphragm packless outlet valve with ¼" Gyrolok tube fitting. It has a delivery pressure range of 28–520 kPa (4–75 psig).

Both the Model 19 and the Model 3500 regulators are available with an optional helium leak rate certification.

2. Two Stage Regulators

This type of regulator performs the same function as a single stage regulator. However, greater accuracy and control of delivery pressure is maintained, and the delivery pressure does not vary as cylinder pressure falls. The following two stage regulators are available from Matheson for use with Prepurified, High Purity, and Extra Dry Grades of nitrogen:

Model No.	Delivery Pressure Range kPa	bar (g)	psig
8L-580	14–104	0.14–1.04	2–15
8-580	28–340	0.28–3.4	4–50
8H-580	69–690	0.69–6.9	10–100
9-580	138–1 720	1.38–17.2	20–250

Regulators Model 3800-580 and 3104-580, with delivery pressure ranges of 28-620 kPa (4-90 psig) and 28-690 kPa (4-100 psig), respectively, are recommended for use with all other grades of nitrogen.

3. Low Pressure Regulator

Sensitive and very accurate low pressure regulation may be obtained with Matheson Model 70 low pressure regulators. The low pressure regulators have oversize pancake bodies of die cast aluminum with Buna N diaphragms. The 70 Models are rated for a maximum inlet pressure of 250 psig. Where the cylinder pressure exceeds 250 psig excellent results are obtained by using a pressure reducing regulator, such as Matheson's Model 1L, and delivering this pressure to the Model 70. When so used, the two regulators can be connected together with a heavy duty hose and the proper fittings, which are available as a unit. The following Model 70 regulators are available from Matheson for use with Prepurified, High Purity, and Extra Dry Grades of nitrogen.

Model No.	Delivery Pressure Range kPa	mbar (g)	psig
70B	0.5–3.0	5–30	2–12 inches water column
70	3.45–34.5	34.5–345	0.5–5.0 psig
70A	34.5–68.9	345–689	5–10 psig

4. Special High Pressure Regulators

The following single stage regulators are recommended for use with nitrogen at 24 130 kPa (3 500 psig).

Model No.	Delivery Pressure Range* kPa	bar (g)	psig
3-580	690–10 340	6.9–103.4	100–1 500
4-580	690–17 240	6.9–172.4	100–2 500
3064-580	172.5–27 600	1.72–276.0	25–4 000
3075-580	1 380–41 370	13.8–413.7	200–6 000

The following single stage regulators are recommended for use with cylinders of nitrogen at 41 370 kPa (6 000 psig):

Model No.	Delivery Pressure Range* kPa	bar (g)	psig
3064-677	172.5–27 600	1.72–276.0	25–400
3066-677	345–41 400	3.45–414.0	50–6 000
3075-677	1 380–41 370	13.8–413.7	200–6 000

Manual Controls

Manual needle valves for direct attachment to the cylinder valve outlet are available. These types of controls are mainly used where intermittent flows are necessary, or where it is desired to control the flow of gas directly from the cylinder. This type of needle valve will allow control of extremely slow flow rates on up to relatively large flow rates. However, pressure cannot be controlled with such a valve, and, if a line or system becomes plugged, dangerous pressures can build up. The following manual type valves are recommended for use with nitrogen in cylinders rated under 24 130 kPa (3 500 psig):

* Maximum delivery pressure is dependent upon gas cylinder pressure.

Model 50-580 and Model 52-580 with gauge to indicate tank pressure. These valves can be supplied with a variety of outlets, such as a hose connection, ¼" tube fitting, or ¼" NPT male or female outlet. Needle valves Models 30AR and 31B are recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass or stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass or stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Nitrogen is shipped in high pressure steel cylinders as a nonflammable compressed gas, taking a DOT "Green Label". The cylinders are usually filled to the marked service pressure of the cylinder or to a maximum of 10% in excess of the marked service pressure, in accordance with present DOT regulations.

Chemical Preparation

Large quantities of nitrogen are produced by the liquefaction and fractionation of air. If the commercial product is to be used in the laboratory, the trace quantities of oxygen usually present can be removed by passing the gas through aqueous solutions containing active reducing agents as V^{2+} or Cr^{2+} or over hot, finely divided copper. Small amounts of very pure nitrogen may be conveniently prepared by thermal decomposition of alkali-metal (except lithium) azides, e.g., $2MM_3 \rightarrow 2M + 3N_2$.

Chemical Properties

Nitrogen is relatively inert to most reagents at ordinary conditions. Elemental nitrogen reacts rapidly with lithium at room temperature to give Li_3N. Elemental nitrogen can be fixed in biological systems at room temperature, but the mechanism of such processes is at present unknown. In addition, certain transition-metal complexes have been shown recently to react rapidly with atmospheric nitrogen.

Nitrogen becomes more reactive at elevated temperatures and combines with hydrogen, oxygen, and some metals: $3H_2 + N_2 \rightarrow 2NH_3$; $O_2 + N_2 \rightarrow 2NO$; $3M + N_2 \rightarrow M_3N_2$ (M = Ca, Mg, Ba).

A very reactive form of nitrogen, active nitrogen, is formed when gaseous nitrogen is passed through a glow discharge at low pressures. Active in nitrogen reacts readily with many metals (Hg, As, Zn, Cd, Na) and nonmetals (P, S) to yield nitrides. For reactions of nitrogen at high temperatures, see reference 2.

Thermodynamic and Detailed Physical Data

Molecular Structure

The homopolar nitrogen molecule has $D_{\infty h}$ symmetry and a symmetry number of two, with a N-N bond distance of 1.087 58 Å (1.087 58 × 10^{-10} m).

Infrared Spectrum

The homopolar diatomic nitrogen molecule has only one vibration along the chemical bond. The vibration is not infrared active but is Raman active.

Vapor Pressure (4)

The vapor pressure of liquid nitrogen between 7.999 kPa (60 mmHg) and 199.984 kPa (1 500 mmHg) is represented by the Antoine vapor pressure equation:

$$\log_{10}p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10}p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.494 57, 255.680, and 266.550, respectively.

Some calculated vapor pressure values are shown below.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
60.81	7.999	80	60
62.286	10.666	107	80
63.486	13.332	133	100
67.570	26.664	267	200
70.242	39.997	400	300
72.285	53.329	533	400
73.962	66.661	667	500
75.397	79.993	800	600
76.659	93.325	933	700
77.352	101.325	1 013.25	760
77.79	106.658	1 067	800
78.82	119.990	1 200	900
79.76	133.322	1 333	1 000
81.46	159.986	1 600	1 200
83.65	199.983	2 000	1 500

For vapor pressure values up to the critical point, see Table 1.

Latent Heat of Vaporization,
ΔHv (3) @ 77.35 °K ..... 5 577.3 J/mol; 1.333 kcal/mol

For Δ Hv values at other temperatures, see Table 1.

Thermodynamic Data

Thermodynamic properties of saturated nitrogen and of superheated nitrogen are shown in Tables 1 and 2, respectively. Molar specific heats and compressibility factors for nitrogen are shown in Tables 3 and 4, respectively.

Thermodynamic Properties of Nitrogen As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	29.125 J/(mol·°K)
Entropy, S°	191.502 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−191.502 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	8.669 kJ/mol
Enthalpy of Formation, ΔH_f°	0.000 kJ/mol
Free Energy of Formation, ΔF_f°	0.000 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of nitrogen, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1976*, Matheson, East Rutherford, New Jersey.

[2] J. H. Hall, in Kirk-Othmer's *Encyclopedia of Chemical Technology*, 2nd edition, 1967, Volume 13, pp. 858–859, John Wiley & Sons, Inc., New York, New York.

[3] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds, 1968*, Volume 1, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[3] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[5] F. Din, *Thermodynamic Functions of Gases*, F. Din, editor, *1961*, Volume 3, p. 139, Butterworth, Inc., Washington, D. C.

[6] **Ibid.**, pp. 158–161.

[7] **Ibid.**, pp. 142–145.

[8] **Ibid.**, pp. 146–150.

[9] **Ibid.**, pp. 151–155.

[10] **Ibid.**, pp. 156–157.

[11] *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p. 3–107, McGraw-Hill Book Co., Inc., New York, New York.

Table 1. PROPERTIES OF THE SATURATED LIQUID AND VAPOR (5)

Temperature		Pressure		Entropy J/(mol·K)		Enthalpy J/mol		Latent Heat of Vaporization J/mol	Specific Volume dm^3/kg		Density kg/m^3	
°K	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
63.15*	−346.0	12.534	0.123 7	68.15	166.40	2 713	8 916	6 203	1.150 1	1 495.574	869.5	0.669
65.89	−341.1	20.265	0.2	70.53	162.75	2 867	8 943	6 076	1.167 5	965.163	856.5	1.036
68.41	−336.5	30.398	0.3	72.64	159.76	3 009	8 969	5 960	1.184 3	664.941	844.4	1.504
71.91	−330.2	50.662	0.5	75.48	156.18	3 208	9 011	5 803	1.202.5	413.014	831.6	2.421
74.45	−325.7	70.928	0.7	77.46	153.93	3 353	9 046	5 693	1 217.9	302.042	821.1	3.311
77.35	−320.4	101.325	1	79.66	151.78	3 522	9 100	5 578	1.237.5	217.376	808.1	4.600
83.80	−308.8	202.650	2	83.98	148.00	3 874	9 239	5 365	1.285 3	113.864	778.0	8.782
88.04	−301.2	303.975	3	86.53	145.81	4 101	9 320	5 219	1.321 0	78.027	757.0	12.82
94.09	−290.3	506.625	5	90.05	143.02	4 443	9 422	4 979	1.379 2	48.865	725.1	20.46
98.60	−282.2	709.275	7	92.71	140.95	4 699	9 455	4 756	1.433 8	35.462	697.4	28.20
103.88	−272.7	1 013.250	10	95.93	138.56	5 035	9 463	4 428	1.505 9	24.875	664.0	40.20
110.57	−260.6	1 519.875	15	100.33	135.42	5 526	9 406	3 880	1.620 5	15.848	617.1	63.10
115.80	−251.2	2 026.500	20	104.25	132.68	5 988	9 280	3 292	1.745 1	11.112	573.0	90.00
120.13	−243.4	2 533.125	25	108.08	130.00	6 444	9 077	2 633	1.901 1	8.063	526.0	124.0
123.86	−236.7	3 039.750	30	112.19	127.06	6 943	8 785	1 842	2.132 0	5.779	469.0	173.0
126.2**	−232.5	3 394.388	33.5	120.00	120.00	7 922	7 922	0	3.215 8	3.215 8	311.0	311.0

* Triple point; **Critical point.

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED NITROGEN

H, ENTHALPY, kJ/mol (6); **S**, ENTROPY, J/(mol·°K) (7); **V**, SPECIFIC VOLUME, m^3/kg (8)

Pressure kPa	atm		Temperature, °K 130	150	170	190	210	230	250	280
		H	10.655	11.239	11.821	12.401	12.980	13.559	14.138	15.007
101.325	1	S	167.10	171.28	174.92	178.15	181.04	183.68	186.09	189.38
		V	0.377 4	0.436 9	0.496 1	0.555 1	0.614 1	0.672 9	0.731 2	0.820 0
		H	10.629	11.219	11.805	12.388	12.969	13.550	14.130	15.001
202.650	2	S	161.22	165.44	169.10	172.34	175.25	177.89	180.30	183.59
		V	0.187 0	0.217 1	0.247 1	0.276 8	0.306 5	0.336 1	0.365 6	0.409 8
		H	10.547	11.155	11.754	12.347	12.935	13.521	14.105	14.980
506.625	5	S	153.16	157.51	161.26	164.56	167.50	170.16	172.59	175.89
		V	0.072 7	0.085 3	0.097 7	0.109 8	0.121 9	0.133 9	0.145 9	0.163 8
		H	10.398	11.040	11.666	12.276	12.877	13.471	14.063	14.946
1 013.250	10	S	146.61	151.20	155.12	158.52	161.52	164.23	166.69	170.03
		V	0.034 5	0.041 3	0.047 9	0.054 2	0.060 4	0.0666	0.072.7	0.081 7
		H	10.235	10.921	11.575	12.204	12.817	13 421	14.020	14.911
1 519.875	15	S	142.36	147.27	151.36	154.86	157.93	160.68	163.18	166.55
		V	0.021 7	0.026 6	0.031 2	0.035 6	0.039 9	0.044 1	0.048 2	0.054 4
		H	9.800	10.663	11.385	12.055	12.696	13.321	12.934	14.843
2 533.125	25	S	135.69	141.80	146.32	150.05	153.26	156.10	158.66	162.09
		V	0.011 0	0.014 8	0.018 0	0.020 8	0.023 5	0.026 2	0.028 8	0.032 6
		H	6.872	9.727	10.840	11.658	12.384	13.064	13.718	14.676
5 066.250	50	S	110.08	131.13	138.15	142.71	146.43	149.43	152.16	155.77
		V	0.001 89	0.005 58	0.007 99	0.009 74	0.001 3	0.012 8	0.014 2	0.016 2
		H	6.558	8.071	9.719	10.860	11.766	12.561	13.306	14.366
10 132.5	100	S	105.67	111.69	127.37	133.73	138.28	141.90	145.00	149.00
		V	0.001 64	0.002 16	0.003 31	0.004 46	0.005 39	0.006 22	0.007 02	0.008 13
		H	6.578	7.780	9.040	10.111	11.069	11.949	12.775	13.940
20 625.0	200	S	102.43	111.09	119.03	125.00	129.80	133.81	137.25	141.66
		V	0.001 50	0.001 74	0.002 08	0.002 47	0.002 87	0.003 28	0.003 70	0.004 28
		H	6.719	7.772	8.855	9.858	10.801	11.686	12.529	13.732
30 397.5	300	S	100.55	108.10	114.88	120.48	125.20	129.23	132.74	137.28
		V	0.001 43	0.001 59	0.001 78	0.002 00	0.002 24	0.002 49	0.002 74	0.003 11
		H	6.895	7.884	8.874	9.836	10.759	11.639	12.480	13.683
40 530.0	400	S	98.95	106.03	112.23	117.58	122.20	126.20	129.71	134.25
		V	0.001 38	0.001 50	0.001 64	0.001 80	0.001 96	0.002 13	0.002 30	0.002 57
		H	7.090	8.045	8.994	9.926	10.830	11.699	12.533	13.728
50 662.5	500	S	97.54	104.37	110.31	115.50	120.03	123.98	127.46	131.97
		V	0.001 34	0.001 44	0.001 55	0.001 67	0.001 79	0.001 92	0.002 06	0.002 27
		H	7.305	8.243	9.171	10.081	10.966	11.823	12.649	13.839
60 795.0	600	S	96.33	103.04	108.85	113.91	118.34	122.24	125.68	130.18
		V	0.001 30	0.001 39	0.001 48	0.001 57	0.001 68	0.001 79	0.001 90	0.002 07
		H	7.761	8.681	9.585	10.469	11.331	12.168	12.980	14.159
81 060.0	800	S	94.27	100.85	106.51	111.42	115.74	119.54	122.93	127.38
		V	0.001 25	0.001 32	0.001 39	0.001 46	0.001 54	0.001 62	0.001 70	0.001 83
		H	8.241	9.151	10.042	10.911	11.758	12.582	13.385	14.555
101 325	1 000	S	92.60	99.12	104.70	109.53	113.76	117.51	120.86	125.27
		V	0.001 21	0.001 26	0.001 32	0.001 39	0.001 45	0.001 51	0.001 58	0.001 68
		H	10.731	11.636	12.517	13.372	14.202	15.008	15.761	16.935
202 650	2 000	S	86.62	93.10	98.62	103.37	107.53	111.20	114.47	118.79
		V	0.001 09	0.001 12	0.001 16	0.001 19	0.001 22	0.001 26	0.001 29	0.001 34
		H	13.108	14.024	14.916	15.783	16.622	17.436	18.227	19.382
303 975	3 000	S	82.17	88.72	94.31	99.13	103.33	107.04	110.34	114.70
		V	0.001 01	0.001 04	0.001 07	0.001 09	0.001 12	0.001 14	0.001 17	0.001 20
		H	15.396	16.320	17.224	18.103	18.957	19.787	20.596	21.775
405 300	4 000	S	78.51	85.12	90.77	95.66	99.94	103.71	107.08	111.53
		V	0.000 968	0.000 989	0.001 01	0.001 03	0.001 05	0.001 07	0.001 09	0.001 12
		H		18.551	19.468	20.364	21.235	22.081	22.906	24.112
506 625	5 000	S		81.96	87.69	92.68	97.04	100.89	104.33	108.89
		V		0.000 950	0.000 968	0.000 985	0.001 00	0.001 02	0.001 03	0.001 06

Temperature, °K 300	340	380	400	450	500	550	600	650	700
15.586	16.746	17.908	18.490	19.946	21.405	22.867	24.332	25.800	27.271
191.37	195.00	198.23	199.72	203.15	206.22	209.01	211.56	213.91	216.08
0.878 7	0.996 1	1.113 5	1.172 1	1.318 8	1.465 3	1.611 9	1.758.5	1.905 0	2.051 5
15.581	16.742	17.905	18.487	19.944	21.404	22.866	24.332	25.800	27.271
185.59	189.23	192.46	193.95	197.38	200.45	203.24	205.79	208.14	210.31
0.439 3	0.498 1	0.556 9	0.586 2	0.659 6	0.733 0	0.806 3	0.879.6	0.952 9	1.026 2
15.563	16.728	17.895	18.478	19.939	21.400	22.864	24.331	25.800	27.272
177.90	181.55	184.79	186.29	189.72	192.80	195.59	198.14	200.49	202.67
0.175 6	0.199 3	0.022 3	0.234 7	0.264 1	0.293 6	0.322 9	0.352 3	0.381 6	0.411 0
15.533	16.705	17.877	18.463	18.928	21.393	22.860	24.329	25.800	27.274
172.06	175.73	178.98	180.48	183.93	187.01	189.80	192.35	194.70	196.88
0.087 7	0.099 7	0.111 6	0.117 5	0.132 3	0.147 1	0.161 8	0.176 5	0.191 2	0.205 9
15.503	16.683	17.860	18.448	19.917	21.386	22.856	24.327	25.799	27.274
168.59	172.28	175.55	177.06	180.52	183.61	186.41	188.97	191.33	193.51
0.058 5	0.066 5	0.074 5	0.078 5	0.088 4	0.098 3	0.108 1	0.177 9	0.127 8	0.137 6
15.444	16.639	17.827	18.419	19.897	21.373	22.848	24.322	25.798	27.276
164.17	167.91	171.21	172.73	176.21	179.32	182.13	184.70	187.06	189.25
0.035 0	0.040 0	0.044 8	0.047 2	0.053 2	0.059 2	0.065 2	0.071 1	0.077 0	0.082 9
15.303	16.535	17.750	18.352	19.850	21.343	22.831	24.316	25.800	27.282
157.94	161.80	165.18	166.72	170.24	173.39	176.22	178.80	181.17	183.37
0.017 5	0.020 1	0.022 6	0.023 8	0.026 9	0.029 9	0.032 9	0.035 9	0.038 9	0.041 9
15.044	16.352	17.616	18.239	19.782	21.308	22.822	24.326	25.825	27.321
151.34	155.41	158.93	160.53	164.16	167.37	170.25	172.87	175.27	177.48
0.008 84	0.010 21	0.011 52	0.012 16	0.013 8	0.015 3	0.016 9	0.018 4	0.019 9	0.021 4
14.679	16.087	17.432	18.090	19.705	21.287	22.844	24.383		
144.21	148.61	152.35	154.04	157.84	161.18	164.15	166.82		
0.004 66	0.005 38	0.006 07	0.006 41	0.007 25	0.008 06	0.008 86	0.009 64	0.010 42	
14.497	15.957	17.351	18.032	19.699	21.325	22.919	24.486		
139.91	144.48	148.35	150.10	154.02	157.44	160.48	163.21		
0.003 36	0.003 84	0.004 32	0.004 55	0.005 12	0.005 67	0.006 21	0.006 74	0.007 27	
14.453	15.934	17.356	18.051	19.751	21.407	23.025	24.613		
136.90	141.53	145.49	147.27	151.27	154.76	157.84	160.60		
0.002 75	0.003 11	0.003 47	0.003 64	0.004 07	0.004 49	0.004 90	0.005 30	0.005 70	
14.497	15.987	17.425	18.128	19.848	21.522	23.158	24.761		
134.62	139.28	143.28	145.08	149.13	152.65	155.76	158.55		
0.002 41	0.002 69	0.002 97	0.003 11	0.003 45	0.003 78	0.004 11	0.004 44	0.004 76	
14.607	16.097	17.539	18.246	19.978	21.664	23.312	24.926		
132.82	137.48	141.49	143.30	147.37	150.92	154.06	156.87		
0.002 19	0.002 42	0.002 65	0.002 76	0.003 04	0.003 32	0.003 60	0.003 87	0.004 14	
14.923	16.411	17.857	18.567	20.311	22.012	23.675	25.303		
130.02	134.68	138.70	140.52	144.62	148.20	151.37	154.20		
0.001 91	0.002 08	0.002 25	0.002 33	0.002 33	0.002 75	0.002 96	0.003 16	0.003 36	
15.315	16.800	18.247	18.959						
127.88	132.51	136.53	138.36						
0.001 74	0.001 88	0.002 01	0.002 08						
17.682	19.147	20.580	21.286						
121.37	125.96	129.94	131.75						
0.001 38	0.001 44	0.001 51	0.001 55						
20.136	21.615	23.062	23.775						
117.30	121.93	125.95	127.78						
0.001 23	0.001 28	0.001 33	0.001 35						
22.544	24.053	25.530	26.258						
114.18	118.90	123.00	124.87						
0.001 14	0.001 18	0.001 21	0.001 23						
24.897	26.441	27.953	28.699						
111.60	116.43	120.64	122.55						
0.001 07	0.001 11	0.001 14	0.001 15						

Table 3. MOLAR SPECIFIC HEAT OF REAL GAS NITROGEN AT CONSTANT PRESSURE (Cp) (9) AND CONSTANT VOLUME (Cv) (10) UNIT: J/(mol•°K)

Pressure kPa	bar	atm		Temperature, °K 130	150	200	250	300	400	500	600	700
101.325	1.013 25	1	Cp	29.27	29.12	28.97	28.95	28.98	29.09	29.21	29.33	29.45
			Cv	20.5	20.5	20.6	20.6	20.6	20.8	20.9	21.0	21.2
1 013.25	10.1	10	Cp	32.80	31.67	30.04	29.48	29.35	29.29	29.32	29.40	29.50
			Cv	20.8	20.7	20.7	20.7	20.7	20.8	20.9	21.0	21.2
2 533.12	25.3	25	Cp	52.4	38.20	32.02	30.48	29.99	29.58	29.50	29.50	29.57
			Cv	21.7	21.2	20.9	20.8	20.7	20.8	20.9	21.0	21.2
5 066.25	50.7	50	Cp		77	36.06	32.39	31.12	30.07	29.80	29.67	29.68
			Cv	24.5	22.1	21.2	20.9	20.8	20.9	20.9	21.0	21.2
10 132.5	101.3	100	Cp	60.9	93	44.72	36.35	33.45	31.05	30.38	30.01	29.92
			Cv	27.0	23.5	21.9	21.4	21.1	21.0	21.0	21.1	21.2
25 331.2	253.3	250	Cp	52.16	60.0	47.25	41.01	37.10	33.29	31.79	30.88	
			Cv	28.0	26.1	23.1	22.2	21.7	21.3	21.3	21.2	
50 662.5	506.6	500	Cp	47.81	47.67	45.18	40.85	38.00	34.89	33.08	31.74	
			Cv	28.8	27.5	24.6	23.3	22.5	21.8	21.6	21.4	
81 060.0	810.6	800	Cp	46.28	45.63	43.03	40.06	37.82	35.32	33.62	32.22	
			Cv	29.6	28.5	25.9	24.1	23.1	22.3	22.0	21.7	
101 325	1 013	1 000	Cp	45.84	45.01	42.33	39.65	37.68	35.39	33.81	32.42	
			Cv	30.1	29.0	26.5	24.6	23.5	22.7	22.2	21.8	

Table 4. COMPRESSIBILITY FACTORS FOR NITROGEN (11)

Temperature, °K	Pressure, kPa 100	500	1 000	2 000	4 000	6 000	8 000	10 000	20 000	30 000	40 000	50 000
70	0.005 7	0.028 7	0.057 3	0.114 3	0.227 7	0.340 0	0.451 6	0.562 3	1.104 4	1.630 8	solid	solid
80	0.959 3	0.026 4	0.052 8	0.105 3	0.209 3	0.312 2	0.414 0	0.514 8	1.006 1	1.479 7	1.939 6	2.387 9
90	0.972 2	0.025 1	0.050 0	0.099 6	0.197 5	0.293 8	0.388 8	0.482 6	0.936 2	1.370 0	1.789 0	2.196 2
100	0.979 8	0.891 0	0.048 7	0.099 6	0.190 5	0.282 3	0.372 0	0.460 5	0.884 0	1.285 2	1.670 7	2.044 1
120	0.988 3	0.939 7	0.873 2	0.705 9	0.197 5	0.282 2	0.364 1	0.443 8	0.818 8	1.168 4	1.501 5	1.822 3
140	0.992 7	0.963 5	0.925 3	0.843 3	0.637 6	0.425 1	0.427 8	0.479 9	0.794 2	1.099 6	1.392 0	1.672 6
160	0.995 2	0.976 6	0.952 9	0.904 2	0.803 1	0.701 7	0.630 4	0.613 4	0.810 7	1.070 8	1.327 5	1.576 2
180	0.996 7	0.984 6	0.969 0	0.938 1	0.878 2	0.812 5	0.778 4	0.753 0	0.855 0	1.066 9	1.289 3	1.510 5
200	0.997 8	0.989 7	0.979 1	0.959 2	0.921 2	0.888 2	0.862 1	0.845 5	0.906 7	1.076 0	1.268 3	1.463 1
250	0.999 2	0.996 0	0.992 4	0.985 7	0.974 1	0.965 5	0.960 4	0.958 9	1.004 8	1.114 3	1.250 1	1.396 2
300	0.999 8	0.999 0	0.998 3	0.997 1	0.996 4	0.997 3	1.000 0	1.005 2	1.055 9	1.142 2	1.248 0	1.362 9
350	1.000 1	1.000 7	1.001 1	1.002 9	1.006 9	1.012 5	1.018 9	1.027 1	1.081 0	1.156 0	1.244 5	1.340 5
400	1.000 2	1.001 1	1.002 4	1.005 7	1.012 5	1.019 9	1.028 3	1.037 7	1.092 9	1.160 9	1.238 2	1.321 6
450	1.000 3	1.001 8	1.003 3	1.007 3	1.015 3	1.023 8	1.033 2	1.043 0	1.097 6	1.160 6	1.230 3	1.304 3
500	1.000 4	1.002 0	1.004 0	1.008 1	1.016 7	1.025 7	1.035 0	1.045 1	1.098 4	1.157 5	1.221 3	1.288 1
600	1.000 4	1.002 1	1.004 0	1.008 4	1.017 3	1.026 3	1.035 5	1.045 0	1.095 1	1.154 0	1.202 8	1.265 7
800	1.000 4	1.001 7	1.003 6	1.007 4	1.015 7	1.023 7	1.032 0	1.040 2	1.083 2	1.126 4	1.170 1	1.214 0
1 000	1.000 3	1.001 5	1.003 4	1.006 7	1.013 6	1.020 5	1.027 5	1.034 7	1.071 4	1.107 8	1.144 9	1.181 4

NITROGEN DIOXIDE

(Synonyms: Dinitrogen Tetroxide; Nitrogen Tetroxide; Nitrogen Peroxide; Liquid Dioxide)
(Formula: NO_2 or N_2O_4)

PHYSICAL PROPERTIES (1)

Molar Mass (NO_2)	
Molecular weight	0.046 005 5 kg
Molar Mass (N_2O_4)	
Molecular Weight	0.092 011 kg
One Mole of NO_2	0.046 005 5 kg
One Mole of N_2O_4	0.092 011 kg
Specific Volume @ 21.1 °C, 101.325 kPa	293.4 dm^3/kg; 4.7 ft^3/lb
Vapor Pressure @ 21.1 °C	101.325 kPa; 14.7 psia; 1 atm
Boiling Point, Equilibrium Mixture @ 101.325 kPa	294.30 °K; 21.2 °C; 70.1 °F
Freezing Point In Air, Equilibrium Mixture @ 101.325 kPa	261.947 °K; −11.2 °C; 11.8 °F
Density, Gas, Equilibrium Mixture @ 101.325 kPa @ 2.11 °C	3.394 kg/m^3
Relative Density, Gas, Equilibrium Mixture @ 101.325 kPa @ 21.1 °C (Air = 1)	2.62
Density, Liquid, Equilibrium Mixture @ 20 °C	1.446 9 kg/l
Critical Temperature, Equilibrium Mixture	431.35 °K; 158.2 °C; 316.8 °F
Critical Pressure, Equilibrium Mixture	10 132.5 kPa; 1 469.6 psia; 100 atm
Critical Volume, Equilibrium Mixture	1.793 dm^3/kg
Critical Density, Equilibrium Mixture	0.557 kg/dm^3
Critical Compressibility Factor, Equilibrium Mixture	0.466
Latent Heat of Fusion, Equilibrium Mixture @ 261.95 °K	14.652 kJ/mol; 3.502 kcal/mol
Dipole Moment, Gas	1.054×10^{-30} C·m; 0.316 D
Specific Heat, Gas, Equilibrium Mixture @ 101.325 kPa, Mean Cp Value @ 27–100 °C	7.11 kJ/(kg·°K); 1.70 kcal/(kg·°K)
Viscosity, Gas, Equilibrium Mixture @ 101.325 kPa @ 26.8 °C	0.014 2 mPa·s; 0.014 2 cP
Viscosity, Liquid, Equilibrium Mixture @ 20 °C	0.42 mPa·s; 0.42 cP
Thermal Conductivity, Gas, Equilibrium Mixture @ 101.325 kPa @ 26.8 °C	0.115 1 W/(m·°K); 275.1×10^{-6} cal·cm/(s·cm^2·°C)
Trouton's Constant, Gaseous NO_2	30.9
Specific Conductivity, Liquid N_2O_4	2.42
Refractive Index, Liquid, n_D @ 20 °C	1.40

Description

Nitrogen dioxide is a red-brown, toxic, paramagnetic gas at room temperature, the latter property being expected because it is a radical. Nitrogen dioxide condenses to a brown liquid, but freezes to a colorless solid. In the process, the system loses its paramagnetism to the point where the solid becomes diamagnetic. This behavior has been interpreted in terms of an equilibrium between monomeric NO_2 and dimeric N_2O_4: $2NO_2 \rightleftharpoons N_2O_4$. The solid is wholly N_2O_4, the liquid contains less than 1% NO_2; and the vapor contains about 90% NO_2 at 373.15 °K (100 °C). Above 413.15 °K (140 °C), the dissociation into NO_2 is complete. Thus, the reported properties of the liquid and gas below 413.15 °K (140 °C) are those of an equilibrium mixture of NO_2 and N_2O_4. X-ray and electron diffraction results indicate that planar N_2O_4 is the most stable conformation of nitrogen dioxide. NO_2 is shipped as a liquefied gas in cylinders and ton containers under its own vapor pressure of 0 kPa (0 psig) at 21.1 °C.

Specifications

Nitrogen dioxide has a minimum purity of 99.5 mole %.

Uses

N_2O_4 has been used as a catalyst in certain oxidation reactions; as an inhibitor to prevent polymerization of acrylates during distillation; as a nitrating agent for organic compounds; as an oxidizing agent; as a rocket fuel; as a flour bleaching agent; in the manufacture of liquid explosives; and for increasing the wet strength of paper.

Effects in Man and Toxicity (2)

Breathing as little as 25 ppm of nitrogen oxides for an 8-hour period may cause pulmonary signs and symptoms after a virtually asymptomatic interval of from 5 to as much as 48 hours. Delayed pulmonary edema may follow exposure to 100–150 ppm for only 30–60 minutes, while a few breaths of the nitrogen oxides in a concentration of 200–700 ppm will produce severe pulmonary damage which may result in fatal pulmonary edema after 5–8 hours or more have elapsed.

The typical sequence of events in poisoning by nitrogen oxides is as follows:

(a) After inhalation of a few breaths of gas, there is no immediate reaction or only very slight respiratory discomfort, headache, dizziness, or lassitude (occasionally nausea and vomiting may appear which usually disappears within 30 minutes; the victim frequently persists in his work;

(b) Five to eight hours after the exposure, perhaps after the worker has returned home, it may be noticed that the victim's lips and ears have become blue (cyanotic);

(c) There follows rapidly increasing difficulty in breathing with accelerated, somewhat irregular respiration, choking, dizziness, headache, increasing cyanosis, a tightness in the chest; and occasionally nausea, vomiting, lassitude, and palpitation also occurs. Untreated cases frequently terminate fatally as a result of pulmonary edema.

Physical examination within a short time after the exposure reveals an accelerated respiratory rate, decreased vital capacity, generally suppressed breath sounds with occasional moist rales and rhonchi, low blood pressure, and an elevated blood platelet count (10–100% above normal); all these signs become more pronounced in inadequately treated cases as time passes.

A severe corrosive action can occur on contact of liquid nitrogen dioxide with the skin or eyes.

In concentrations of 10–20 ppm by volume in air, the nitrogen oxides have pungent odors but are only slightly irritating to the mucous membranes of the upper respiratory tract. The warning power thus is low even though the odors are distinct in concentrations as low as 5 ppm. Only in concentrations above 100 ppm by volume in air do they cause immediate distress.

The 1979 ACGIH has established a Threshold Limit Value of 5 ppm (9 mg/m^3) for nitrogen dioxide*.

First Aid and Medical Treatment (2)

Inhalation

General

It is most important to realize that prompt, efficient treatment during the asymptomatic period may completely avert the delayed, serious, and sometimes fatal, sequelae of pulmonary injury caused by inhalation of the nitrogen oxides. The main objective of the treatment is to provide an adequate supply of oxygen to the tissues so as to prevent, or at least to minimize, the development of pulmonary edema. Oxygen must be supplied as soon as possible in amounts adequate to maintain the normal color of the skin and mucous membranes. A physician should be called immediately and the nature of the injury explained to him.

Specific Actions

Terminate the exposure immediately. If encountered shortly after exposure, instruct the victim to breathe maximally, i.e., as hard and fast as possible. Carry the victim (do not allow him to walk) to an uncontaminated atmosphere and loosen the clothing around the neck and chest to facilitate breathing. Enforce complete bed rest for 24 to 48 hours, whether toxic symptoms and signs are recognized or not, and keep the victim comfortably warm. As soon as there is any indication of poisoning (coughing, difficulty in breathing, or fatigue), start oxygen therapy. Pure oxygen should be administered by any method which insures high inspiratory concentrations. An oronasal mask is usually best. A slightly positive gas pressure is desirable. Inhalation of oxygen should not exceed 1 hour of continuous treatment. After 1 hour oxygen therapy may be interrupted. It may be reinstituted as the clinical condition indicates. A small dose of morphine (e.g., 10×10^{-6} kg) is safe and desirable to diminish anxiety and dyspnea. Frothy exudate from the respiratory tract should be removed by some appropriate means (suctioning, postural drainage, use of antifoaming agents). Most drugs are ineffective and possibly harmful; in this category are atropine, epinephrine, expectorants, emetics, sedative drugs (except for small doses of morphine), and usually cardiac glycosides.

In a few instances, rapid digitalization with a drug like ouabain may be advisable. An emergency tracheostomy under local anesthesia may make it possible to remove foam more efficiently by a suction catheter, but it usually complicates the administration of oxygen. Artificial respiration may become necessary, but unless airway obstruction can be corrected, it is seldom effective. Penicillin and/or other antibiotics should be given in large doses as soon as evidence of a respiratory infection appears. Steroid therapy has been recommended to minimize the inflammatory reaction and to prevent pulmonary fibrosis. Prednisone has been given to exposed adults in amounts of 30×10^{-6} to 80×10^{-6} kg daily in divided doses.

Contact With Eyes

If liquid nitrogen oxides or high concentrations of vapor contact the eyes, they should be thoroughly irrigated with large amounts of water for at least 15 minutes. The eyelids should be held apart during the irrigation to insure contact of water with all of the tissues of the surface of the eyes and lids. If pain is still present, the irrigation should be continued for an additional 15 minutes. As a first aid measure, 2 or 3 drops of a 0.5% pontocaine solution may then be instilled in the eyes. An ophthalmologist should be consulted at once.

Contact With Skin

Remove all contaminated clothing under an emergency shower. Wash the affected skin areas under running water with soap and water for at least 15 minutes. Subsequent medical treatment is the same as for thermal burns.

* 1979 ACGIH Notice of Intent to Change to 3 ppm (6 mg/m^3).

Precautions in Handling and Storage

1. N_2O_4 should be handled only in a well-ventilated area, preferably a hood with forced ventilation.
2. Self-contained breathing apparatus should be available in convenient locations in emergencies.
3. Areas in which N_2O_4 is being handled should be provided with enough exits to permit personnel to leave quickly in case of trouble.
4. Personnel should have available for immediate use, gas masks with Universal canisters for emergencies. These canisters are satisfactory only for short exposures (about 5 minutes for a 2% concentration of N_2O_4, 20 mintues for a concentration of 0.5%) and should be changed on an exact time schedule.
5. Instant-acting safety showers and eye-washing facilities should be available.
6. Personnel handling N_2O_4 should be provided with, and wear, chemical safety goggles and/or a full face shield and rubber gloves.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Small leaks of N_2O_4 in lines or equipment may be detected by means of wet blue litmus paper or starch-iodide paper. Large leaks of N_2O_4 will be evident by their red color. There are also monitoring devices on the market which keep a continuous check on the atmospheric concentration of N_2O_4.

Disposal of Leaking Cylinders

Should it become necessary to dispose of N_2O_4 from a leaking cylinder, the following procedure may be used. Move the cylinder to a hood or safe out-of-doors area. Attach an appropriate needle valve with a long piece of flexible tubing to the cylinder valve and run the liquid N_2O_4 into excess 5–10% aqueous sodium hydroxide solution at a moderate rate. Transfer the resulting solution to the plant disposal unit for neutralization and disposal.

Materials of Construction

N_2O_4 when dry (0.1% moisture or less) is not corrosive to mild steel at ordinary temperatures and pressures. Numerous metals and alloys such as carbon steel, stainless steel, aluminum, nickel, and Inconel are satisfactory for handling and storage. Under wet conditions, stainless steels resistant to about 60% nitric acid serve best. Equipment parts such as valve stems and blower shafts which are partly in contact with the atmosphere should be stainless steel with sufficient chromium content to resist corrosion caused by leaks through stuffing boxes. Good quality ceramic bodies and Pyrex are satisfactory for handling wet or dry N_2O_4. Among the plastics, Teflon and Kel-F films are most satisfactory. Koroseal and Saran are useful but have a limited service life. In general, the vinyl plastics do not hold up well with N_2O_4. Asbestos and asbestos-graphite are satisfactory for valve stuffing boxes. Koroseal has given reasonably good service in this use. For use on pipe threads, graphite-disodium silicate (water-glass) is recommended and hydrocarbon lubricants should be avoided.

Cylinder and Valve Description

N_2O_4 is shipped in DOT approved, low pressure, steel cylinders. Cylinders of N_2O_4 are equipped with Compressed Gas Association (CGA) No. 660 stainless steel diaphragm valves, the approved alternate standard. The value outlet is 1.030″ in diameter with right-hand external threads, with a connector having a flat seat or washer (see Figure 1 for an illustration).

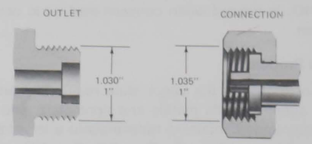


Fig. 1. CONNECTION 660 1.030″-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders of N_2O_4 have no safety devices. They should, therefore, be stored away from sources of heat to prevent dangerous hydrostatic pressures from developing within the cylinder.

Recommended Controls

Manual Controls

Manual needle valve Model 61A-660, of type 303 stainless steel with ¼″ tube fitting, is recommended for use with cylinders of N_2O_4.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

N_2O_4 is classified by the DOT as a "Class A" poison gas, and is shipped with the required "Poison Gas Label".

Commercial Preparation

High quality N_2O_4 is obtained in connection with the production of sodium nitrate from sodium chloride and nitric acid. It is also obtained when sodium nitrite is treated with nitric acid and the evolved NO combined with oxygen; by treating nitrosyl chloride with oxygen to give N_2O_4 and chlorine; by passing ammonia and air heated to 600°C. over a platinum catalyst and treating the NO formed with oxygen to give N_2O_4. Nitrogen dioxide, NO_2 is formed when concentrated nitric acid reacts with copper.

Chemical Properties

Nitrogen dioxide in the vapor state reacts primarily as an oxidizing agent towards metals and nonmetals, and also towards compounds containing nonmetals in a lower oxidation state e.g., $2Cu + NO_2 \rightarrow Cu_2O + NO$; $C + NO_2 \rightarrow CO_2 + \frac{1}{2}N_2$; $7H_2 + 2NO \rightarrow 2NH_3 + 4H_2O$; $X_2 + 2NO \rightarrow 2XNO_2$ (X = Cl, Br); $CO + NO_2 \rightarrow CO_2 + NO$; $SO_2 + NO_2 \rightarrow SO_3 + NO$; $ClNO + NO_2 \rightarrow ClNO_2 + NO$.

With powerful oxidizing agents, higher oxides of nitrogen are formed, e.g., $O_3 + 2NO_2 \rightarrow N_2O_5 + O_2$; $NO_3 + NO_2 \rightarrow N_2O_5$; $H_2O_2 + 2NO_2 \rightarrow 2HNO_3$; $ClNO_2 + 2NO_2 \rightarrow ClNO + N_2O_5$.

In addition, NO_2 has been shown to nitrate aliphatic hydrocarbons in the vapor phase and to add to unsaturated compounds, e.g., $2RH + 4NO_2 \rightarrow 2RNO_2 + H_2O + N_2O_3$; $R_2C = CR_2 + 2NO_2 \rightarrow R_2C = CR_2 \cdot 2NO_2$.

However, liquid dinitrogen tetroxide, which still is an oxidizing agent, undergoes reactions in which the products have a different chemical character. For example, metals react to form nitrates, as do salts which contain oxidizing anions:

$$M + N_2O_4 \rightarrow MNO_3 + NO \ (M = Na, Ag, Cu);$$

$$KN_3 + N_2O_4 \rightarrow KNO_3 + N_2 + N_2O; \ NaClO_3 + N_2O_4 \rightarrow NaNO_3 + NO_2 + ClO_2.$$

NO_2 undergoes thermal decomposition at elevated temperatures: $NO_2 \rightleftarrows NO + \frac{1}{2} O_2$. The decomposition is slight at ordinary temperatures but appreciable above 600 °C. NO_2 reacts with water forming nitric and nitrous acids, the latter decomposing, especially with increased temperature, to nitric acid and nitric oxide.

Thermodynamic and Detailed Physical Data

Molecular Structure

Nitrogen dioxide is a bent triatomic molecule with C_{2v} symmetry and a symmetry number of two, with a N—O bond distance of 1.197 Å (1.197×10^{-10} m) and an O—N—O bond angle of 134.25°. In N_2O_4, the structural parameters are: N—O and N—N bond distances of 1.180 Å (1.180×10^{-10} m) and 1.750 Å (1.750×10^{-10} m), respectively; O—N—O bond angle 133.7°. N_2O_4 has V_h symmetry and a symmetry number of four.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous $NO_2 \rightleftarrows N_2O_4$ equilibrium mixture.

Vapor Pressure (3)

The vapor pressure of the liquid equilibrium mixture from 252.15 °K to 309.65 °K is represented by the following Antoine vapor pressure equation:

$$\log_{10} p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 8.917 12, 1 798.54, and 276.80, respectively.

Some calculated vapor pressure values are shown below.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
252.77	10.666	107	80
256.36	13.332	133	100
268.19	26.664	267	200
275.63	39.997	400	300
281.15	53.329	533	400
285.59	66.661	667	500
289.32	79.993	800	600
292.55	93.325	933	700
294.30	101.325	1 013.25	760
295.41	106.658	1 067	800
297.97	119.990	1 200	900
300.31	133.322	1 333	1 000
304.34	159.986	1 600	1 200
309.63	199.983	2 000	1 500

For additional vapor pressure data, see Figure 3 (vapor pressure curve).

Latent Heat of Vaporization, Equilibrium Mixture (3) @ 294.30 °K	38.116 kJ/mol; 9.110 kcal/mol

Thermodynamic Properties of Nitrogen Dioxide As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	36.974 J/(mol·°K)
Entropy, S°	239.923 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−239.923 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - F_0^\circ$	10.188 kJ/mol
Enthalpy of Formation, ΔH_f°	33.095 kJ/mol
Free Energy of Formation, ΔF_f°	51.241 kJ/mol

Thermodynamic Properties of Dinitrogen Tetroxide As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	77.258 J/(mol·°K)
Entropy, S°	304.277 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−304.277 J/(mol·°K)
Enthalpy difference, $H_{298}^\circ - H_0^\circ$	16.397 kJ/mol
Enthalpy of Formation, ΔH_f°	9.079 kJ/mol
Free Energy of Formation, ΔF_f°	97.717 kJ/mol

Thermodynamic Properties of Liquid Dinitrogen Tetroxide @ 25 °C (4)

Heat Capacity, C_p°	142.507 J/(mol·°K)
Entropy, S°	209.229 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−209.229 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	25.246 kJ/mol
Enthalpy of Formation, ΔH_f°	−19.564 kJ/mol
Free Energy of Formation, ΔF_f°	97.412 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of nitrogen dioxide, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 110–115, Matheson, Lyndhurst, New Jersey.

[3] B. J. Zwolinski, **et al.**, *Selected Values of Properties of Chemical Compounds, 1968*, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[4] **JANAF Thermochemical Tables**, 2nd edition, D. R. Stull and H. Prophet, project directors, *1971*, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U.S. Government Printing Office, Washington, D. C.

[5] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

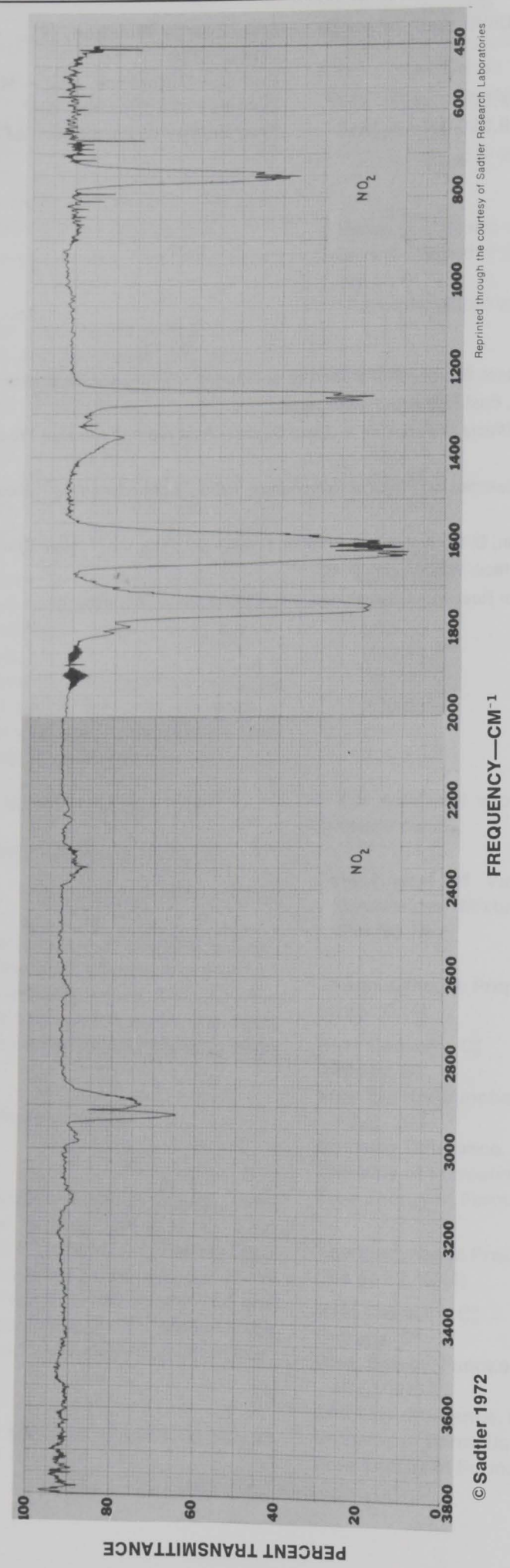
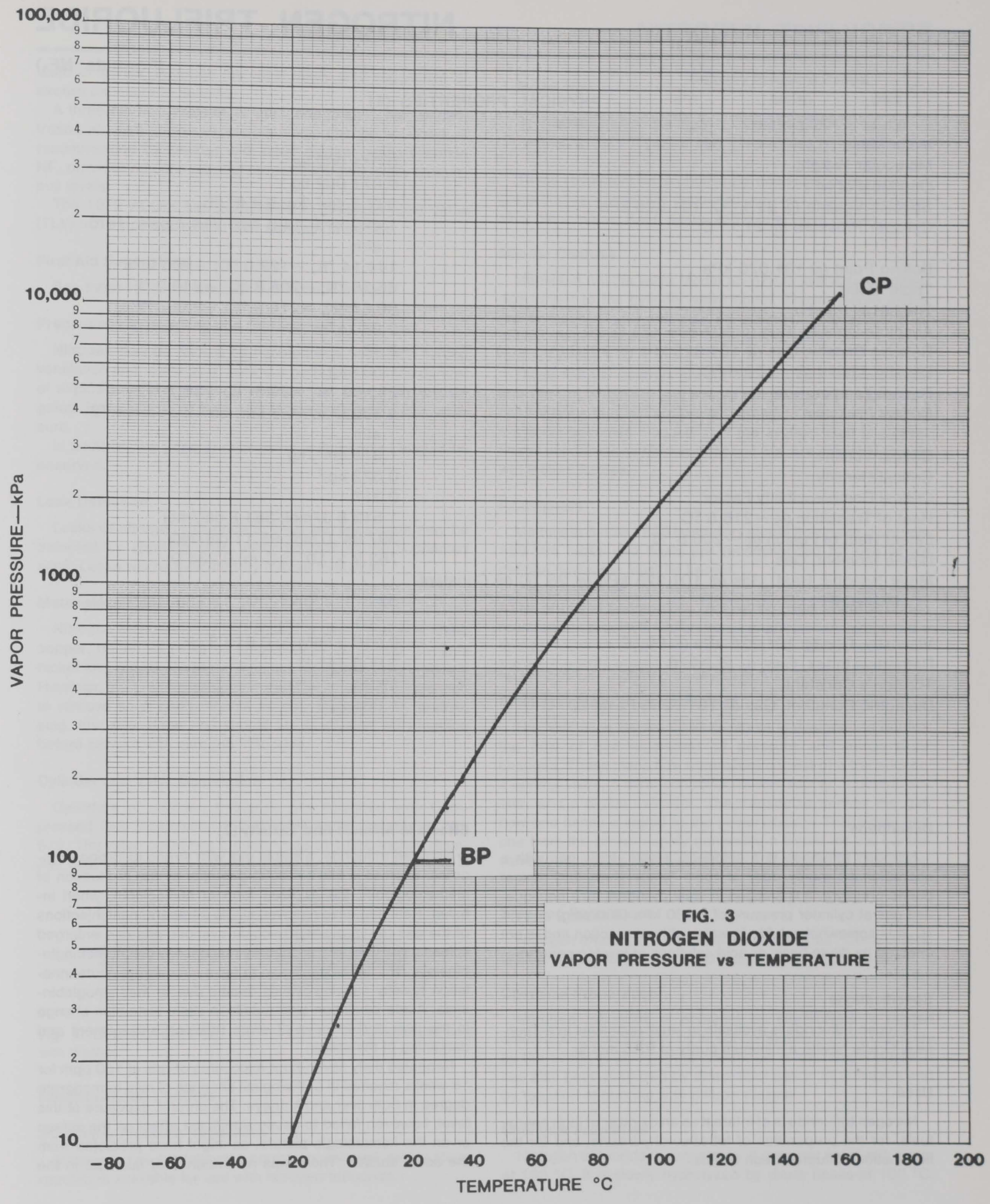


Fig. 2. Infrared spectrum of gaseous NO_2 – N_2O_4 equilibrium mixture over the frequency range of 3 800 cm^{-1} to 450 cm^{-1}; 10-cm path length cell, with KBr optics; cell pressure (complete scan): 1.067 kPa (8 mmHg) (5).

Matheson



Matheson

NITROGEN TRIFLUORIDE

(Formula: NF_3)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.071 002 kg
One Mole of NF_3	0.071 002 kg
Specific Volume @ 21.1 °C, 101.325 kPa	337.1 dm^3/kg; 5.4 ft^3/lb
Cylinder Pressure @ 21.1 °C	1 480 kPa; 14.8 bar; 214.7 psia; 14.6 atm
Boiling Point @ 101.325 kPa	144.14 °K; −129.0 °C; −200.2 °F
Triple Point	66.36 °K; −206.8 °C; −340.2 °F
Transition Point	56.61 °K; −216.5 °C; −355.8 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	2.96 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20°C (Air = 1)	2.46
Density, Liquid @ −129.0 °C	1.531 kg/l
Critical Temperature	233.89 °K; −39.3 °C; −38.7 °F
Critical Pressure	4 530 kPa; 45.3 bar; 657.2 psia; 44.72 atm
Critical Volume	1.915 dm^3/kg
Critical Density	0.522 kg/
Critical Compressibility Factor	0.317
Heat of Transition @ −216.5 °C	1 513.8 J/mol; 361.8 cal/mol
Latent Heat of Fusion @ −206.8 °C	397.94 J/mol; 95.11 cal/mol
Dipole Moment, Gas	783.9 × 10^{-33} C·m; 0.235 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	53.371 J/(mol·°K); 12.756 cal/(mol·°C)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.018 3 mPa·s; 0.018 3 cP
Refractive Index, Gas, n_D @ 25 °C	1.000 441 6
Trouton's Constant	19.94
Dielectric Constant, Gas @ 101.325 kPa @ 20 °C	1.001 275

Description

Nitrogen trifluoride is a colorless, stable, toxic gas with a characteristic moldy odor at room temperature and atmospheric pressure. It is shipped in steel cylinders as a nonliquefied gas at cylinder pressure of 1 380 kPa (200 psig) at 21.1 °C. It is somewhat soluble in water without reaction and is not affected by dilute basic or acid solutions at low temperatures.

Specifications

Nitrogen trifluoride is available in small quantities in a Technical Grade having a minimum purity of 97.5 mol %.

Uses

Nitrogen trifluoride is of interest as an oxidizer of high energy fuels, for the preparation of tetrafluorohydrazine, and for the fluorination of fluorocarbon olefins.

Effects In Animals And Toxicity (2)

Nitrogen trifluoride, a stable gas with strong oxidizing properties, expresses this oxidizing potential by the production of methemoglobin, the oxidized form of hemoglobin, when inhaled. Rats that have received single intraperitoneal injections of the gas (8–15 mg/kg) become cyanotic and had enlarged spleens, possibly as a secondary response to the methemoglobinemia. NF_3 has been shown to have a moderate acute inhalation toxicity causing anoxic deaths due to methemoglobinemia. Acute inhalation also results in slight histologic change in the liver and kidneys of some rats and enlargement and darkening of the spleen.

Repeated daily seven-hour exposures of rats at 100 ppm for 18 weeks resulted in pathological changes of mild to moderate degree in both liver and kidneys. The chronic exposure at this level, however, failed to cause significant effect on the spleen or on the hematologic picture, as might have predicted from the acute studies. There was no evidence of fluorosis in the

teeth or bones, although the renal injury was suggestive of excess exposure to fluoride.

A threshold limit value of 10 ppm, one-tenth of the concentration at which demonstrable histologic change occurred, is recommended by analogy with other oxidant gases because NF_3 provides no odor-warning properties at potentially dangerous levels.

The 1979 ACGIH has established a Threshold Limit Value (TLV) of 10 ppm (30 mg/m^3) for nitrogen trifluoride.

First Aid Suggestions

See those recommended for hydrogen fluoride.

Precautions in Handling and Storage

Nitrogen fluoride should be handled in a hood with forced ventilation and, preferably, behind a barricade until the danger of explosion of the particular reaction has been fully investigated. Heat, shock, or blast can detonate it when under pressure.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks of nitrogen trifluoride in lines and equipment may be detected by applying soap water solution to the suspected sites. Leaks will be indicated by bubble formation.

Materials of Construction

Nitrogen trifluoride may be handled in glass, stainless steel, copper, monel, or nickel at temperatures up to 200 °C. Only nickel and monel are recommended for higher temperatures. However, the process equipment must be scrupulously cleaned to remove such contaminants as dirt, moisture, oil, grease, slag, and pipe dope and should be passivated with fluorine before contact with nitrogen trifluoride.

Cylinder and Valve Description

Cylinders of nitrogen trifluoride are equipped with Compressed Gas Association (CGA) valve outlet connection No. 679. The valve outlet has a thread size of 1.030 inches diameter (see Figure 1).

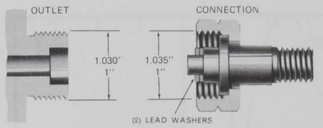


Fig. 1. CONNECTION 679 1.030"-14 LH EXT. using Small Flat Seat with Washer

Recommended Controls

Automatic Pressure Regulators

Matheson has the following corrosion resistant, single stage regulators available for use with nitrogen trifluoride.

Model No.	Delivery Pressure Range		
	kPa	bar(g)	psig
B15-679	28–345	0.28–3.45	4–50
B16-679	345–4 480	3.45–44.8	50–650

These regulators have chemically deposited pure nickel on brass bodies, chemically deposited pure nickel on nickel-silver alloy diaphragms, Kel-F seats, and monel valve outlets.

Manual Controls

Matheson needle valve Model 55-679 is available for direct attachment to the cylinder valve outlet. These needle valves are of monel stock, and may be equipped with a variety of outlets (hose connection, ¼" tube fitting, or ¼" NPT male or female outlet.)

These manual controls should be used only where manual flow control is needed and should not be used as a pressure control since they will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. Monel needle valves Models 33M and 60L are available for use wth lecture bottles.

Flowmeters

Matheson Series 7600 laboratory monel flowmeter units with 150 mm tubes and floats are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 of monel construction, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8260 of monel is designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Nitrogen trifluoride is classified by the DOT as "Compressed Gases, n.o.s." and takes a DOT label: "Flammable Gas".

Chemical Preparation

Nitrogen trifluoride is obtained by electrolysis of molten ammonium bifluoride and by direct combination of the elements by the action of an electrical discharge at low temperatures. It has also been prepared by direct fluorination of ammonia and by reaction of fluorine with difluorodiazine.

Chemical Properties

Nitrogen trifluoride is very stable. It does not react with water at 133 °C. It is slowly hydrolyzed by dilute bases at 100 °C.

Nitrogen fluoride reacts with various metals, such as copper, bismuth, arsenic, antimony, stainless steel, and mercury, at elevated temperatures (around 350 °C.) to form tetrafluorohydrazine. Nitrogen fluoride reacts with hexafluoropropylene over sodium fluoride at 520 °C. to give mainly iso-C_3 to C_6-fluorocarbons and fluorocarbon imines. Nitrogen fluoride reacts with hexafluoropropylene over cesium fluoride at 320 °C. to give, as major products, $(CF_3)_2CFCF(CF_3)_2$, $(CF_3)_2CFNF_2$, and $(CF_3)_2C{:}NF$. Although nitrogen trifluoride is a strong oxidizing agent, it is surprisingly inert at ordinary temperatures.

Thermodynamic and Detailed Physical Data

Molecular Structure

Nitrogen trifluoride is a pyramidal molecule, having C_{3v} point group symmetry and a symmetry number of three. The N—F bond distance is 1.371 Å (1.371×10^{-10} m) and a F—N—F bond angle of 102.15°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous nitrogen trifluoride.

Vapor Pressure

The vapor pressure of liquid nitrogen trifluoride over the temperature range of 102.15–154.65 °K is represented by the following equation (3):

$$\log_{10} p = 6.779\,66 - \frac{501.93}{T - 15.37}$$

in which p = mmHg and T = °K.

Some calculated vapor pressure values are shown below.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
102.15	1.333	13.3	10
106.95	2.666	26.7	20
112.30	5.333	53.3	40
115.71	7.999	80.0	60
118.28	10.666	107	80
120.37	13.332	133	100
127.43	26.664	267	200
132.02	39.997	400	300
135.50	53.329	533	400
138.36	66.661	667	500
140.79	79.993	800	600
142.93	93.325	933	700
144.09	101.325	1 013.25	760
144.83	106.658	1 067	800
146.56	119.990	1 200	900
148.15	133.322	1 333	1 000
150.99	159.986	1 600	1 200
154.65	199.983	2 000	1 500

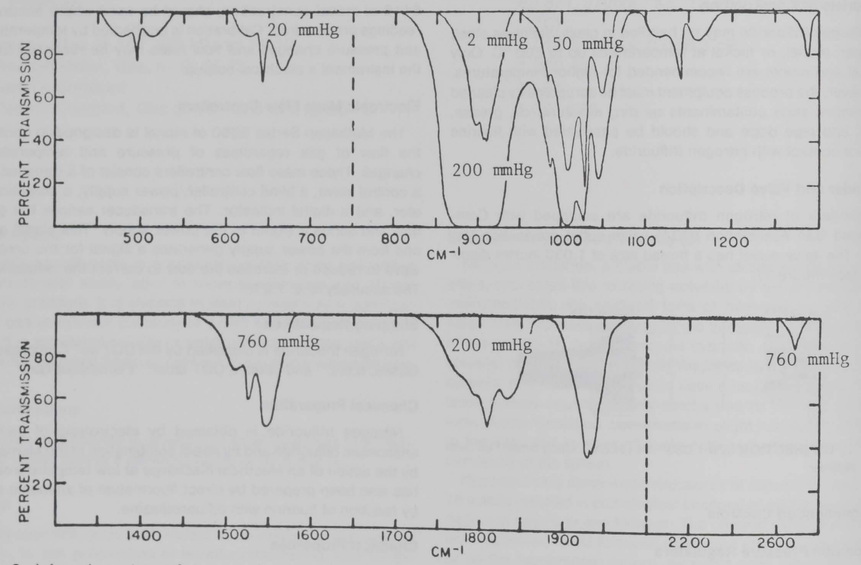


Fig. 2. Infrared spectrum of gaseous nitrogen trifluoride; in the range from 750 cm^{-1} to 3 000 cm^{-1}, the spectrum was measured in a 10-cm gas cell and a spectrometer equipped with NaCl optics; in the range from 400 cm^{-1} to 750 cm^{-1}, the spectrum was measured in an 85-cm gas cell and a spectrometer equipped with KBr optics; cell pressures are shown in the figure (5).

The vapor pressure from 144.5 °K up to the critical point (233.89 °K) is represented by the following equation (3):

$$\log_{10} P = 4.272\,64 - \frac{613.33}{T}$$

in which P = atm and T = °K.

Some calculated values are shown below.

Temperature, °K	Vapor Pressure kPa	bar	atm
171.62	506.625	5.07	5
187.41	1 013.250	10.1	10
206.40	2 026.500	20.3	20
219.40	3 039.750	30.4	30
229.66	4 053.000	40.5	40
233.90	4 531.254	45.3	44.72

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv

Temperature, °C	ΔHv, kJ/mol
−93.0	14.075
−113.0	12.485
−129.0	11.585

Thermodynamic Properties of Nitrogen Trifluoride As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	53.371 J/(mol·°K)
Entropy, S°	260.659 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−260.659 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	11.849 kJ/mol
Enthalpy of Formation, ΔH_f°	−131.503 kJ/mol
Free Energy of Formation, ΔF_f°	−90.019 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of nitrogen trifluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] T. R. Torkelson, *et al.*, *Tox. & Appl. Pharm.* 4, 770 (1962).

[3] R. H. Jarry and H. C. Miller, *J. Phys. Chem.* 60, 1412–1413 (1956).

[4] *JANAF Thermochemical Tables*, 2nd edition, D. R. Stull and H. Prophet, project directors, *1971*, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[5] E. L. Pace and L. Pierce, *J. Chem. Phys.* 23, 1248–1250 (1955).

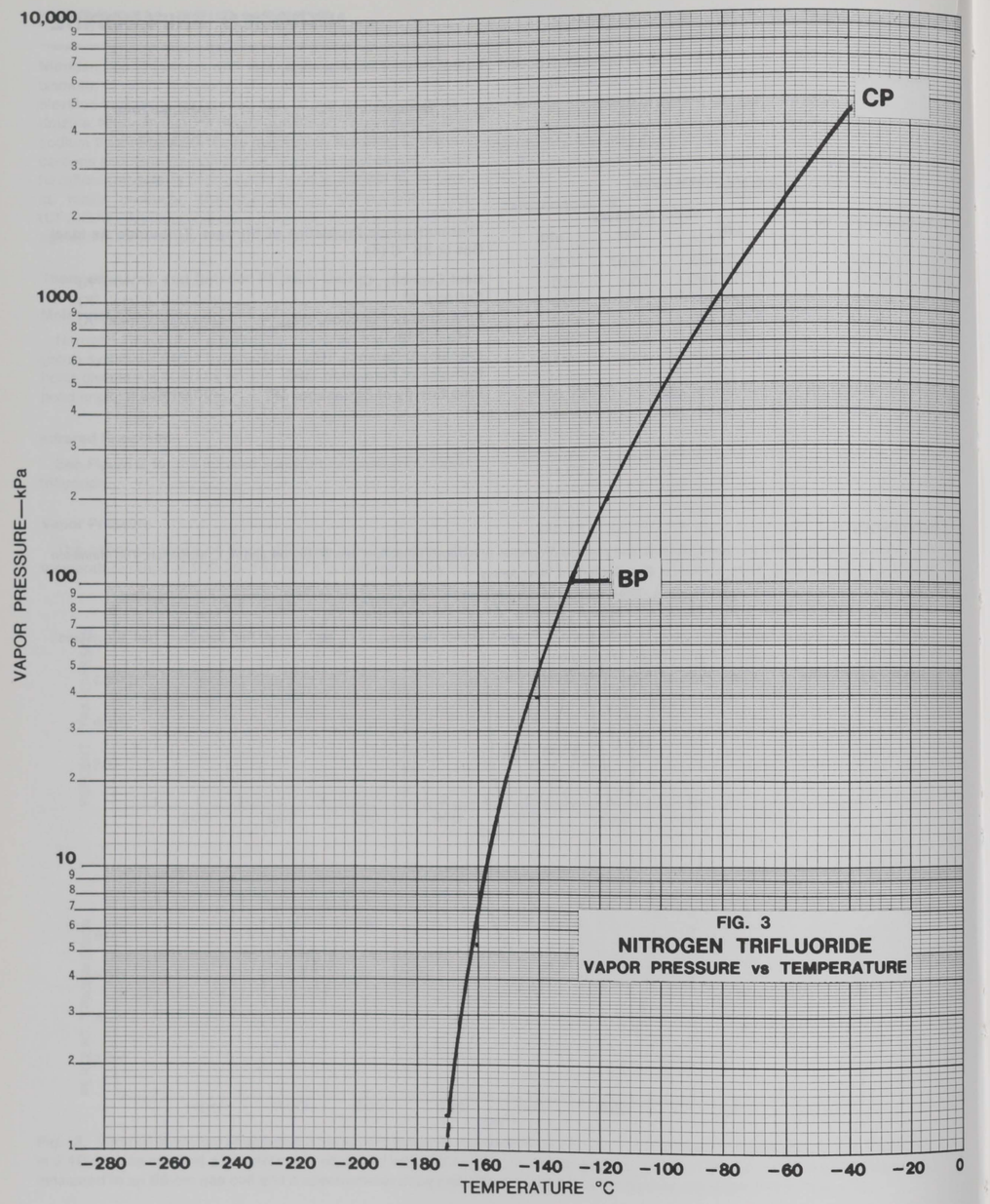


FIG. 3
NITROGEN TRIFLUORIDE
VAPOR PRESSURE vs TEMPERATURE

Matheson

NITROGEN TRIOXIDE

(Synonyms: Dinitrogen Trioxide, Nitrogen(III)Oxide)
(Formula: N_2O_3)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.076 012 kg
One Mole of N_2O_3	0.076 012 kg
Vapor Pressure @ 21.1 °C	2 170 kPa; 21.7 bar; 314.7 psia; 21.4 atm
Boiling Point @ 101.325 kPa	243.15 °K; −30.0 °C; −22.0 °F
Triple Point	172.45 °K; −100.7 °C; −149.3 °F
Density, Liquid @ −30.0 °C	1.447 kg/l
Latent Heat of Fusion, Equilibrium Mixture of NO,NO_2, N_2O_3, and N_2O_4 @ −27.2 °C	58.58 kJ/mol; 14.0 kcal/mol

Description

Nitrogen trioxide has a blue color in the liquid and solid states. Nitrogen trioxide can be prepared by mixing NO and NO_2 below 173.15 °K (−100 °C). The equilibrium $N_2O_3 \rightleftharpoons NO + NO_2$ is achieved at 253.15 °K (−20 °C) with about 10% N_2O_3 being present at 298.15 °K (25 °C) (1). Nitrogen trioxide is shipped in steel cylinders, the cylinder pressure being 2 070 kPa (300 psig) at 21.1 °C

Specifications

Nitrogen trioxide has a minimum purity of 99.0%.

Uses

Nitrogen trioxide with alkalis gives pure alkali nitrites. It is also useful as an oxidant in special fuel systems. Nitrogen trioxide has been used in the identification of terpenes.

Toxicity and First Aid Suggestions

A worker exposed to nitrous fumes should be removed at once to the open air and given absolute rest. *He must remain quiet even though he has apparently recovered.* If coughing continues he should be given oxygen at once and continuously. Do not attempt to help the victim to breathe by artificial respiration, unless his breathing has ceased. A doctor should see the victim as soon as possible. The poisoned worker should be watched for 24 hours even if he feels better temporarily.

Threshold Limit Value (TLV)

No TLV has been established for nitrogen trioxide. Consideration should be given to the TLVs set for nitric oxide (25 ppm) and nitrogen dioxide (5 ppm) as established by the 1979 ACGIH.

In the gaseous state at room temperature, nitrogen trioxide is largely dissociated into NO and $NO_2 \rightleftharpoons N_2O_4$. Reference to data sheets on NO and $NO_2 \rightleftharpoons N_2O_4$ should be made wherein the physiological effects are more fully described. It is recommended that the First Aid Suggestions described in these data sheets should also be applied for nitrogen trioxide.

Precautions in Handling and Storage

Because of its toxic nature, nitrogen trioxide should be handled and stored only in a dry, cool, well-ventilated area, and preferably fire-resistant; a hood with forced ventilation should be used wherever possible. Personnel should wear gas masks, chemical safety goggles or full face shields and rubber gloves when handling nitrogen trioxide. Nitrogen trioxide cylinders should preferably be cooled before withdrawing the material as a liquid. Nitrogen trioxide should be withdrawn only as a liquid to prevent dissociation to $NO_2 \rightleftharpoons N_2O_4$ and NO.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks in lines and vessels in which nitrogen trioxide is being used may be detected with moist blue litmus paper which will turn pink in the presence of nitrogen trioxide, or with moist starch-iodide paper which will turn blue.

Disposal of Leaking Cylinders

Leaking cyclinders of nitrogen trioxide may be disposed of as follows. Put on an appropriate gas mask or breathing equipment. Transfer cylinder to a hood and cool in ice-water. Attach appropriate needle valve with piece of suitable flexible tubing to the cylinder valve. Run the liquid nitrogen trioxide into excess 10% aqueous sodium hydroxide solution. Transfer to plant disposal unit for neutralization and disposal.

Materials of Construction

When wet, nitrogen trioxide is corrosive to steel, but with a moisture content of 0.1% or less, steel is satisfactory. Wet or dry nitrogen trioxide may be handled in 18-8 stainless steels.

Matheson

Cylinder and Valve Description

Nitrogen trioxide is shipped in DOT approved steel cylinders. Cylinders of nitrogen trioxide are equipped with Compressed Gas ASsociation (CGA) alternate standard No. 660 stainless steel diaphragm valves. The valve outlet is 1.030" in diameter with right-hand external threads, with a connector having a flat seat and a washer (see Figure 1 for an illustration).

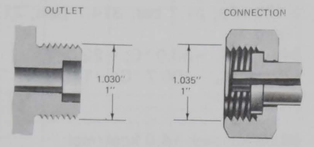


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders of nitrogen trioxide contain no safety devices.

Recommended Controls

Manual Controls

Matheson supplies needle valve Model 61A-660, of type 303 stainless steel, for withdrawal of liquid nitrogen trioxide.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%

Shipping Regulations

Nitrogen trioxide is classified by the DOT as a "Class A Poison" liquid and is shipped under a "Poison Gas Label".

Chemical Preparation

Dinitrogen trioxide, N_2O_3, a blue solid, can be prepared by mixing NO and NO_2 below −100 °C. The equilibrium $N_2O_3 \rightleftarrows NO + NO_2$ is achieved at −20 °C with about 10% N_2O_3 being present at 25 °C.

Chemical Properties

Alkalis absorb nitrogen trioxide forming nitrites. Sulfuric acid absorbs nitrogen trioxide forming nitrosyl sulfuric acid. The reactions of olefins with nitrogen trioxide and nitrogen dioxide have been reviewed by Riebsomer (2).

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

Nitrogen trioxide has C_s point group symmetry and a symmetry number of one. The structural parameters are as follows: bond distances: N-N 2.08 Å (2.08×10^{-10} m); N-O (nitroso) 1.12 Å (1.12×10^{-10} m); N-O (nitro) 1.18 Å (1.18×10^{-10} m); bond angles: O-N-N (nitroso) 110°; O-N-O 134°. ^{14}N nmr experiments on liquid N_2O_3 and other experiments suggest an oxygen-bridged structure, ONONO, for N_2O_3.

Thermodynamic Properties of Nitrogen Trioxide As Ideal Gas @ 25 °C (3)

Heat Capacity, C_p°	65.618 J/(mol·°K)
Entropy, S°	309.60 J/(mol·°K)
Free Energy Function, $(F^\circ_{298} - H^\circ_{298})/298$	−309.60 J/(mol·°K)
Enthalpy Difference, $H^\circ_{298} - H^\circ_{0^\circ}$	11.042 kJ/mol
Enthalpy of Formation, H_f°	82.843 kJ/mol
Free Energy of Formation, F_f°	139.428 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of nitrogen trioxide, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] J. L. Riebsomer, *Chem. Rev.* 36, 196 (1945).

[3] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

NITROSYL CHLORIDE

(Formula: NOCl)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.065 459 kg
One Mole of NOCl	0.065 459 kg
Specific Volume @ 21.1 °C, 101.325 kPa	368.3 dm^3/kg; 5.9 ft^3/lb
Vapor Pressure @ 21.1 °C	288 kPa; 2.88 bar; 41.7 psia; 2.84 atm
Boiling Point @ 101.325 kPa	267.77 K; −5.4 °C; 22.3 °F
Triple Point	213.55 K; −59.6 °C; −75.3 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	2.741 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	2.31
Density, Liquid @ Saturation Pressure @ −12 °C	1.417 kg/l
Critical Temperature	440.65 °K; 167.5 °C; 333.5 °F
Critical Pressure	9 120 kPa; 91.2 bar; 104.7 psia; 90 atm
Critical Volume	2.14 dm^3/kg
Critical Density	0.47 kg/dm^3
Critical Compressibility Factor	0.35
Latent Heat of Fusion @ −59.6 °C	5.983 ± 0.753 kJ/mol; 1.430 ± 0.180 kcal/mol
Dipole Moment, Gas	6.104×10^{-30} C·m; 1.83 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	45.190 J/(mol·°K)
Molar Specific Heat, Liquid @ 0 °C	62.993 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.011 56 mPa·s; 0.011 56 cP
Viscosity, Liquid @ −20 °C	0.547 mPa·s; 0.547 cP
Surface Tension @ −5.5 °C	30.3 mN/m; 30.3 dyn/cm
Dielectric Constant, Liquid @ 19.5 °C	21.4
Specific Conductivity, Liquid @ 10 °C	$2.7 \times 10^{-6}\ \Omega^{-1}$/cm

Description

At room temperature and atmospheric pressure nitrosyl chloride is a reddish-brown, nonflammable, toxic gas having an irritating odor. It is readily liquefied and is shipped in nickel or monel cylinders as a liquefied gas under its own vapor pressure of 186 kPa (27 psig) at 21.1 °C.

Nitrosyl chloride is nonexplosive but dissociates into nitric oxide and chlorine with increasing temperature. This dissociation is only 0.63% at 25 °C, but 50% at 300 °C.

Specifications

Nitrosyl chloride has a minimum purity of 97 mole %.

Uses

Nitrosyl chloride is of use in the diazotization, nitrosation, and chlorination of organic compounds. It is also used as a maturation agent.

Effects in Man and Toxicity (2)

The toxicity of nitrosyl chloride has not been thoroughly investigated. It is stated that cats exposed 20 minutes to a concentration of 100 ppm died with evidence of lung injury, and that it can cause fatal pulmonary edema in man and is highly irritating to the skin, eyes and mucous membranes.

On contact with moisture, nitrosyl chloride is hydrolyzed to hydrochloric acid and nitrous acid, the latter decomposing at body temperature giving rise to nitrogen oxides (nitric oxide and nitrogen dioxide). Consequently, the effects produced by exposure to nitrosyl chloride will be the result of the combined effects of hydrochloric acid and nitrogen oxides. For the individual effects of these gases, the sections on Hydrogen Chloride and Nitrogen Oxides should be consulted. The highly irritating odor of the vapors of nitrosyl chloride should be taken as a warning of the presence of dangerous concentrations.

Threshold Limit Value (TLV)

No TLV has been established for nitrosyl chloride. The TLVs of hydrogen chloride, nitric oxide, and nitrogen dioxide* are 3, 25 and 5 ppm, respectively.

First Aid Treatment (2)

It is suggested that the first aid procedures described for exposure to hydrogen chloride and nitrogen oxides be followed.

* 1979 ACGIH Notice of Intent to Change to 3 ppm (6 mg/m^3).

Precautions in Handling and Storage

Personnel handling or using nitrosyl chloride should do so only in a well-ventilated area, preferably a hood with forced ventilation. Personnel should wear NIOSH approved full-face gas masks and rubber gloves when handling or using nitrosyl chloride. Airline or oxygen masks or self-contained breathing apparatus should be conveniently located for emergencies. Instant-acting safety showers and eye-washing facilities should be readily available.

Suckback may cause a violent reaction within the cylinder, and may lead to the formation of extremely corrosive conditions; therefore, to prevent suckback a check valve, vacuum break, or trap should be employed when using nitrosyl chloride.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks of nitrosyl chloride in lines and equipment may be detected by means of moist blue litmus paper, or by exposing a squeeze bottle containing aqueous ammonia to the suspected areas.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-D.

Materials of Construction

Lines and valves must be kept clean and dry inside and out to prevent accumulation of moisture, which leads to very rapid corrosion.

Under pressure, nickel, monel, or Inconel should be used for all connectors, adapters, valves, and pressure gauges.

Piping and equipment to contain nitrosyl chloride should be of nickel, monel, Inconel, tantalum, platinum, or glass. Also lead, Koroseal, and Saran pipe are satisfactory for use at room temperature and slightly above atmospheric pressure. Threaded and flanged pipe joints should be of nickel, monel, or Inconel. A caulking compound of water glass and powdered graphite is satisfactory for threaded joints. Gaskets of softened "L" nickel, sheet asbestos, and lead may be used for flanged joints.

Under moist conditions, nitrosyl chloride is handled best in tantalum or glass.

Cylinder and Valve Description

Nitrosyl chloride is shipped in DOT approved, low pressure nickel or monel cylinders. Cylinders containing nitrosyl chloride are equipped with Compressed Gas Association (CGA) cylinder valve outlet connection No. 660, the approved alternate connection (see Figure 1 for illustration). No. 7N cylinders have a special $\frac{5}{16}$"-32 threads per inch female outlet.

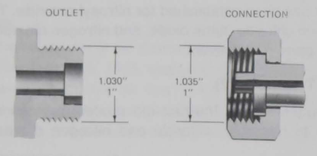


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

Safety Devices

No safety devices are required in cylinders containing less than 10 lbs of nitrosyl chloride. Cylinders containing nitrosyl chloride should, therefore, be stored away from sources of heat to prevent dangerous hydrostatic pressures from developing within the cylinder.

Recommended Controls

Monel needle valve Model 55A-660 with ¼" tube fitting is recommended for use with No. 4N cylinders of nitrosyl chloride. This needle valve can be attached directly to the cylinder valve outlet. Manual needle valve Model 601, of monel, is recommended for use with No. 7N cylinders of nitrosyl chloride.

Flowmeters

Matheson Series 7600 laboratory monel flowmeter units with 150 mm tubes and floats are recommended for use where definite flow rates must be known.

Monel electronic mass flowmeters, such as Matheson Series No. 8116, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8260 of monel is designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control value to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Nitrosyl chloride is classified by the DOT as a nonflammable gas, taking a "Green Label."

Commercial Preparations

Nitrosyl chloride is produced commercially as a co-product of chlorine and sodium nitrate by the reaction of sodium chloride and nitric acid. It can also be prepared by a variety of procedures, e.g., by reaction of nitrogen dioxide with moist potassium chloride or moist sodium chloride, by direct combination of nitric oxide and chlorine, from hydrogen chloride and nitrosylsulfuric acid, from sodium chloride and nitrosylsulfuric acid, etc.

Chemical Properties

Nitrosyl chloride reacts rapidly with water to form nitrous and hydrochloric acids. Nitrosyl chloride forms addition compounds, such as $(NO)ZnCl_6$, etc. Nitrosyl chloride reacts with oxygen in the gas phase quite slowly at temperatures below

200 °C; in free space at 1 atm., nitrosyl chloride is rapidly oxidized at 300 °C and above giving nitrogen dioxide and chlorine. Sulfur dissolved in sulfur monochloride reacts with nitrosyl chloride at 100 °C and normal pressure in the presence of ferric chloride to give sulfur monochloride and nitric oxide. Nitrosyl chloride in the presence of water reacts with aromatic amines to form diazonium chlorides. Nitrosyl chloride acts as a chlorinating agent toward hydrocarbons in the vapor phase at elevated temperatures at atmospheric pressure. Under proper conditions, nitrosyl chloride adds to olefins giving nitroso chlorides.

In the presence of strong Lewis acids, NOCl acts as a Cl^- donor, forming nitrosonium salts:

$$NOCl + MCl_3 \rightarrow NOMCl_4$$

$$(M = B,Al,Ga,In,Tl,Bi,Fe,Au)$$

$$2NOCl + MCl_4 \rightarrow (NO)_2MCl_6$$

$$(M = Sn,Ti,Pb,Pt).$$

Nitrosonium salts of hexafluoro-anions ($NOMF_6$, M = P, As, Sb, V) have also been prepared. A variety of other nitrosonium salts are available through double decomposition reactions in other nonaqueous solvents. Nitrosonium salts are rapidly hydrolyzed, giving solutions of nitrous acid, which can be regarded as a very weak base:

$$NO^+ + 2H_2O \rightarrow H_3O^+ + HNO_2$$

$$HONO \rightleftharpoons HO^- + NO^+.$$

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

Nitrosyl chloride is a bent triatomic molecule, with C_s point group symmetry and a symmetry number of one. The structural parameters are as follows: bond distances: Cl-N 1.95 Å (1.95 × 10^{-10} m); N-O 1.17 Å (1.17 × 10^{-10} m); bond angle: Cl—N—O 114 ± 3°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous nitrosyl chloride.

Vapor Pressure (4)

The vapor pressure of nitrosyl chloride between 213.15 °K and 285.05 °K is represented by the Antoine vapor pressure equation:

$$\log_{10}p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10}p} - C$$

in which t = °C and p = mmHg, and the constants A, B, and C have the values of 7.361 54, 1 094.73, and 249.70, respectively.

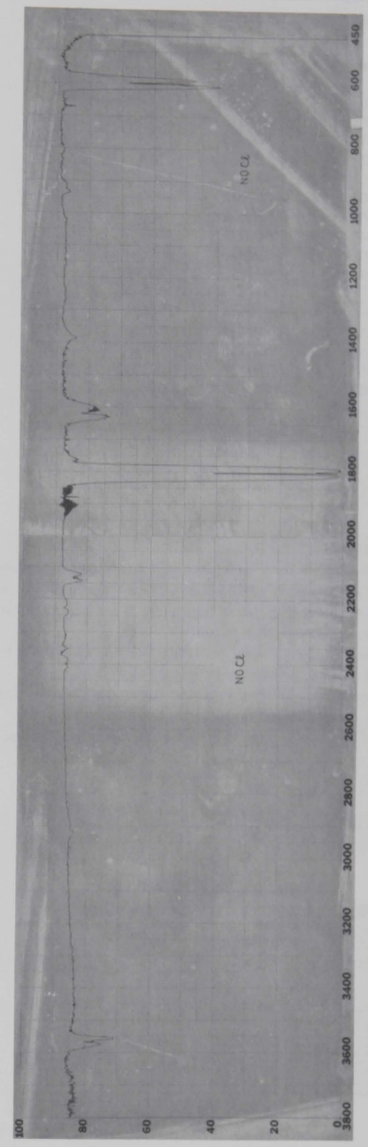


Fig. 2. Infrared spectrum of gaseous nitrosyl chloride; 10-cm path length cell, with KBr windows; cell pressure (complete scan): 0.667 kPa (5 mmHg) (5).

NITROSYL CHLORIDE

Some calculated vapor pressure values are shown below.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
213.55	5.333	53.33	40
219.55	7.999	80.0	60
224.01	10.666	107	80
227.63	13.332	133	100
239.78	26.664	267	200
247.58	39.997	400	300
253.46	53.329	533	400
258.24	66.661	667	500
262.30	79.993	800	600
265.84	93.325	933	700
267.77	101.325	1 013.25	760
268.99	106.658	1 067	800
271.85	119.990	1 200	900
274.45	133.322	1 333	1 000
279.05	159.986	1 600	1 200
285.05	199.983	2 000	1 500

For vapor pressure values to the critical point, see Figure 3.

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/mol
240.15	27.179
267.77	25.690
293.15	24.188

Thermodynamic Properties of Nitrosyl Chloride As Ideal Gas @ 25 °C (3)

Heat Capacity, C_p°	44.685 J/mol·°K)
Entropy, S°	261.613 J/(mol·°K)
Free Energy Function, $(F^\circ_{298} - H^\circ_{298})/298$	−261.613 J/(mol·°K)
Enthalpy Difference, $H^\circ_{298} - H^\circ_0$	11.351 kJ/mol
Enthalpy of Formation, ΔH_f°	51.756 kJ/mol
Free Energy of Formation, ΔF_f°	66.107 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of nitrosyl chloride, see W. Braker and A. L. Mossman. *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 117–119, Matheson, Lyndhurst, New Jersey.

[3] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D.C.

[4] B. J. Zwolinski, et al., *Selected Values of Properties of Chemical Compounds, 1968*, Volume 1, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[5] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

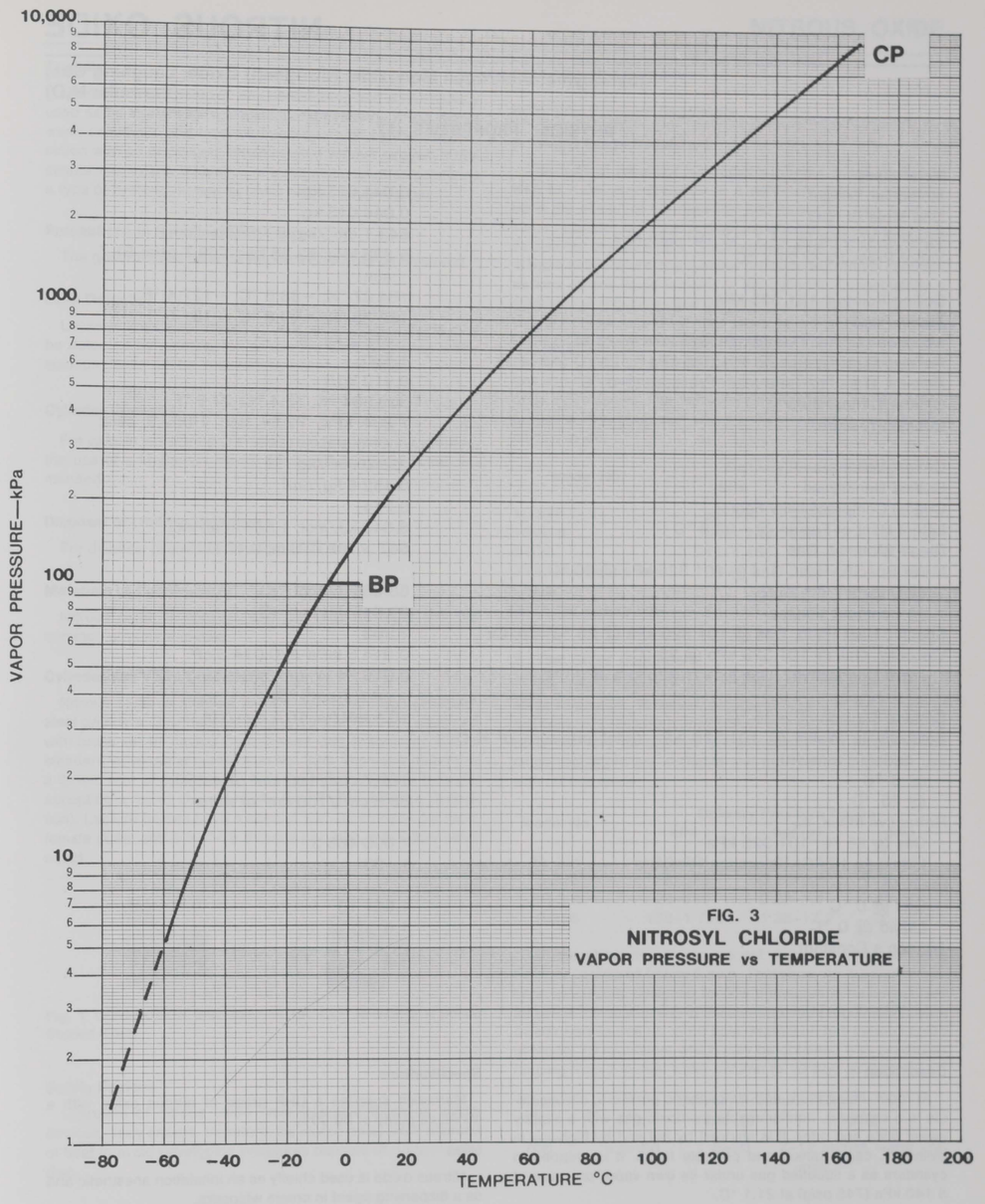


FIG. 3
NITROSYL CHLORIDE
VAPOR PRESSURE vs TEMPERATURE

NITROUS OXIDE

(Synonyms: Dinitrogen Monoxide; Nitrogen(I) Oxide; Laughing Gas)
(Formula: N_2O)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.044 013 kg
One Mole of N_2O	0.044 013 kg
Specific Volume @ 21.1 °C, 101.325 kPa	543.1 dm^3/kg; 8.7 ft^3/lb
Vapor Pressure @ 21.1 °C	5 238 kPa; 52.38 bar; 759.7 psia; 51.7 atm
Boiling Point @ 101.325 kPa	184.67 °K; −88.5 °C; −127.4 °F
Triple Point	182.33 °K; −90.8 °C; −131.5 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	1.812 2 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.530
Density, Liquid @ Saturation Pressure @ 0 °C	0.913 kg/l
Critical Temperature	309.584 °K; 36.4 °C; 97.6 °F
Critical Pressure	7 254 kPa; 72.54 bar; 1 052.2 psia; 71.6 atm
Critical Volume	2.210 dm^3/kg
Critical Density	0.452 5 kg/dm^3
Critical Compressibility Factor	0.274
Latent Heat of Fusion @ −90.8 °C	6.540 kJ/mol; 1.563 kcal/mol
Dipole Moment, Gas	567 × 10^{-33} C.m; 0.17 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	38.635 J/(mol·°K)
@ Constant Volume	29.648 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.303
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.014 5 mPa·s; 0.014 5 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.016 74 W/(m·°K); 40.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −25 °C	10.1 mN/m; 10.1 dyn/cm
Solubility in Water @ 101.325 kPa (total pressure of N_2O + aqueous tension)	
@ 0 °C	129.7 cm^3/100 cm^3 of water
@ 25 °C	58.8 cm^3/100 cm^3 of water
Refractive Index, n_D	
Gas @ 25 °C, 101.325 kPa	1.000 465 3
Liquid @ 16 °C, Saturation Pressure	1.193
Dielectric Constant	
Gas @ 0 °C	1.001 13
Liquid @ 0 °C	1.61
Trouton's Constant	21.4

Description

At room temperature and atmospheric pressure, nitrous oxide is a colorless, nonflammable, nontoxic gas with a slightly sweet taste and odor. It is shipped by rail and by highway in cylinders, cargo tanks, and portable tanks. It is shipped in cylinders as a liquefied gas under its own vapor pressure of 5 140 kPa (745 psig) at 21.1 °C.

Specifications

Matheson supplies a UHP grade of nitrous oxide with a minimum purity of 99.99%.

Uses

Nitrous oxide is used chiefly as an inhalation anesthetic and as a dispersing agent in cream whippers.

Matheson

Toxicity

Nitrous oxide is nontoxic and nonirritating and is extensively used as an anesthetic in medicine and dentistry. It is a rather weak anesthetic and must be inhaled in high concentrations, mixed with air or oxygen. When inhaled without oxygen, it is a simple asphyxiant. Inhalation of small amounts often produces a type of hysteria; hence its trivial name, "laughing gas."

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Leak Detection

Leaks in lines and equipment to contain nitrous oxide may be detected by painting the suspected sites with soap water solution; leaks will be indicated by bubble formation.

Cylinder Contents

For ease in monitoring the nitrous oxide content in cylinders, the use of a Matheson Model 8510 cylinder scale is recommended.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-C.

Materials of Construction

Nitrous oxide is noncorrosive and may be used with the common structural metals.

Cylinder and Valve Description

Nitrous oxide is shipped in DOT approved, high pressure, steel cylinders. Cylinders containing nitrous oxide are equipped with brass valves having Compressed Gas Association (CGA) standard valve outlet connection No. 326. The valve outlet has a thread size of 0.825 inch, with right-hand external threads, accepting a round shaped nipple (see Figure 1 for an illustration). Lecture bottles have a special 5/16"-32 threads per inch, female outlet and a 9/16"-18 threads per inch, male dual valve outlet.

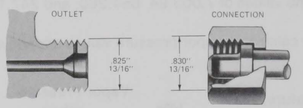


Fig. 1 CONNECTION 326 .825"-14 RH EXT. accepting a Round Shaped Nipple

Safety Devices

Cylinders of nitrous oxide have frangible discs as safety devices. They should, therefore, be stored away from sources of heat to avoid developing pressures capable of rupturing the disc.

Recommended Controls

Automatic Pressure Regulators

1. Single Stage Regulators

The type of regulator will reduce cylinder pressure in one step to a delivery pressure in a particular range depending upon the design of the regulator and its spring load. A single stage regulator will show a slight variation in delivery pressure as cylinder pressure falls. Since nitrous oxide is a liquefied gas at room temperature, the cylinder pressure will remain constant as long as any liquid remains in the cylinder. Consequently a single stage regulator used with nitrous oxide will give a steady delivery pressure and cylinder pressure will not vary until the liquid phase has been exhausted. Above its critical temperature of 36.5 °C (97.7 °F) nitrous oxide will convert completely to a gas and the discharge of cylinder contents will show a steady drop in pressure. The following single stage regulators are available from Matheson and are recommended for use with nitrous oxide:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
1L-326	28–550	0.28–5.5	4–80
1H-326	69–1 240	0.69–12.4	10–180
2-326	345–4 480	3.45–44.8	50–650
3320 (for lecture bottles)	28–410	0.28–4.1	4–60
3321 (for lecture bottles)	28–410	0.28–4.1	4–60

2. Two Stage Regulators

This type of regulator performs the same function as single stage regulators. However, greater accuracy in the control of the delivery pressure is maintained and the delivery pressure does not vary as cylinder pressure falls. The following two stage regulators are available and are recommended for use with nitrous oxide:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
8L-326	14–104	0.14–1.04	2–15
8-326	28–345	0.28–3.45	4–50
8H-326	28–340	0.28–3.4	4–50
9-326	138–1 720	1.38–17.2	20–250

All the above regulators are not satisfactory for accurate delivery pressures below 5 psig. Therefore, an auxiliary regulator specifically designed for low pressures is recommended for use in series with any of the standard type regulators having delivery pressures up to 80 psig. Matheson has various types of Model 70 regulators which may be obtained with pressures ranging from 2 inches water column to 10 psig as follows:

Model No.	Delivery Pressure Range		
	kPa	mbar (g)	psig
70B	0.5–3.0	5–30	2–12 inches water column

Matheson

Model No.	Delivery Pressure Range kPa	mbar (g)	psig
70	3.45–34.5	3.45–345	0.5–5.0 psig
70A	34.5–68.9	345–689	5–10 psig

When any of the above regulators are used in conjunction with a standard regulator, an extra heavy hose is available to connect to the standard regulator. All Matheson regulators are provided with needle valves attached to the outlets so that accurate flow control can be maintained.

To prevent possible icing of regulator parts and hence possible loss of control, the use of a Matheson Model 6284-326 Nitrous Oxide Heater is recommended between the cylinder valve and regulator.

Manual Controls

Matheson needle valves Models 50-326 and 52-326 with tank gauge, both of brass bar stock, are available for direct attachment to the cylinder valve outlet. Either valve can be equipped with a variety of outlets, such as a hose connection, ¼″ tube fitting, or ¼″ NPT male or female pipe. These valves should be used only where manual flow control is needed and should not be used to control pressure since dangerous pressures can be built up if a system becomes clogged or if the system itself is closed. Needle valves Model 30AR or Model 31B are recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Nitrous oxide is classified by the DOT as a nonflammable, compressed gas and is shipped with the required "Green Label".

Commercial Preparations

Nitrous oxide is obtained most commonly by the thermal decomposition of ammonium nitrate. It may also be obtained by controlled reduction of nitrites or nitrates, by the slow decomposition of hyponitrites, and by the thermal decomposition of hydroxylamine.

Chemical Properties

Nitrous oxide is stable and comparatively unreactive at ordinary temperatures, e.g., to ozone, hydrogen, the halogens, the alkali metals, etc. At elevated temperatures N_2O decomposes into nitrogen and oxygen, the rate of decomposition being appreciable at about 600 °C. At elevated temperatures N_2O supports combustion and oxidizes certain organic compounds, the alkali metals, etc. N_2O is soluble in alkaline solutions but does not form hyponitrites. A crystalline hexahydrate can be obtained at low temperatures.

Thermodynamic And Detailed Physical Data

Molecular Structure (2)

Nitrous oxide is a linear but unsymmetrical molecule having $C_{\infty v}$ point group symmetry and a symmetry number of one. The structural parameters are as follows: bond distances: N—N 1.28 2 Å (1.128×10^{-10} m); N—O 1.184 2 Å ($1.184\ 2 \times 10^{-10}$ m); bond angle: 180°. Various physical measurements indicate that N_2O is a resonance hybrid involving the canonical structures $\ddot{N}{::}\dot{N}{::}\ddot{O}:$ and $:N{:::}\dot{N}{:}\ddot{O}:$.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous nitrous oxide.

Vapor Pressure (3)

The vapor pressure of liquid nitrous oxide between 180.15 °K and 197.15 °K is represented by the following Antoine vapor pressure equation:

$$\log_{10} p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 7.003 94, 654.260, and 247.16, respectively.

Some calculated vapor pressure values are shown below.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
180.82	79.993	800	600
183.31	93.325	933	700
184.67	101.325	1 013.25	760
185.53	106.658	1 067	800
187.55	119.990	1 200	900
189.39	133.322	1 333	1 000
192.69	159.986	1 600	1 200
196.91	199.983	2 000	1 500

For vapor pressure data up to the critical point, see Figure 3.

Latent Heat of Vaporization, ΔHv (3) @ 184.67 °K	16.552 kJ/mol; 3.956 kcal/mol

For additional ΔHv values, see Table 1.

Thermodynamic Data

See Table 1 for the thermodynamic properties of saturated nitrous oxide.

Thermodynamic Properties of Nitrous Oxide As Ideal Gas @ 25 °C (2)

Heat Capacity, C_p°	38.618 J/(mol·°K)
Entropy, S°	219.852 J/(mol·°K)
Free Energy Function, $(F^\circ_{298} - H^\circ_{298})/298$	−219.852 J/(mol·°K)
Enthalpy Difference, $H^\circ_{298} - H^\circ_0$	9.581 kJ/mol
Enthalpy of Formation, ΔH_f°	82.048 kJ/mol
Free Energy of Formation, ΔF_f°	104.165 kJ/mol

REFERENCES

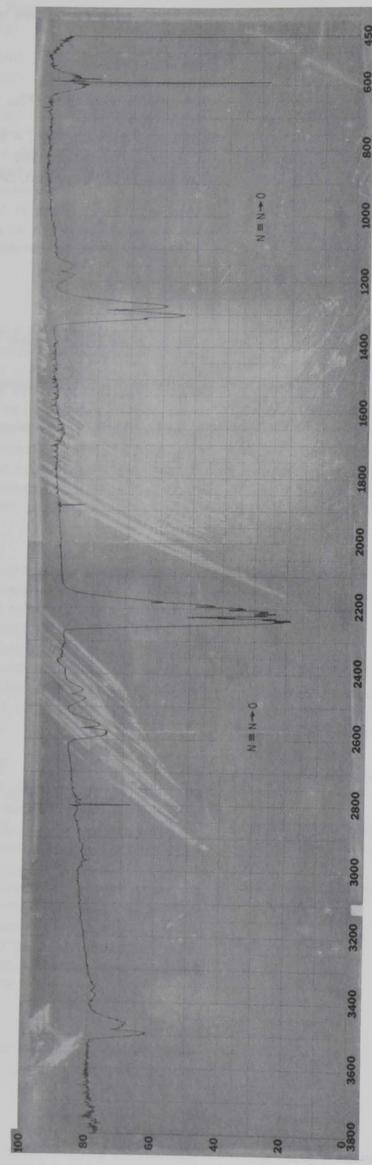
[1] For extensive tabulations of the thermodynamic and physical properties of nitrous oxide, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data. Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[3] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds*, *1968*, Volume 1, Thermodynamic Research Center, Texas A & M University, College Station, Texas.

[4] *The Sadtler Standard Spectra*, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[5] *Amer. Soc. Refrigerating Engineering Data Book*, *1957–1958*.



Reprinted through the courtesy of Sadtler Research Laboratories
©Sadtler 1972

Fig. 2. Infrared spectrum of gaseous nitric oxide; 10-cm path length cell, with KBr windows; cell pressure (complete scan) 5.333 kPa (40 mmHg) (4).

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED NITROUS OXIDE (5)

Temperature		Pressure		Enthalpy kJ/mol		Latent Heat of Vaporization kJ/mol	Specific Volume m^3/kg		Density kg/m^3	
°K	°F	kPa	atm	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
184.82	−127	101.325	1.00	−10.077	6.527	16.604	0.000 78	0.343 4	1 281.5	2.912
188.71	−120	131.000	1.29	−9.883	6.599	16.482	0.000 79	0.265 3	1 265.5	3.769
194.26	−110	179.264	1.77	−9.596	6.721	16.317	0.000 81	0.198 5	1 241.4	5.038
199.82	−100	241.317	2.38	−9.279	6.824	16.103	0.000 82	0.148 6	1 217.4	6.729
205.37	−90	317.159	3.13	−8.921	6.957	15.878	0.000 83	0.113 6	1 201.4	8.803
210.93	−80	399.896	3.95	−8.563	7.049	15.612	0.000 84	0.089 3	1 185.4	11.198
216.48	−70	510.212	5.04	−8.164	7.161	15.325	0.000 86	0.071 8	1 161.3	13.928
222.04	−60	627.423	6.19	−7.755	7.233	14.988	0.000 89	0.058 4	1 129.3	17.123
227.59	−50	772.213	7.62	−7.346	7.315	14.661	0.000 90	0.046 9	1 110.1	21.322
233.15	−40	944.582	9.32	−6.906	7.386	14.292	0.000 92	0.037 8	1 089.3	26.455
238.71	−30	1 151.42	11.36	−6.466	7.438	13.904	0.000 93	0.032 0	1 073.2	31.250
244.26	−20	1 399.64	13.81	−6.005	7.489	13.494	0.000 95	0.026 5	1 049.2	37.736
249.82	−10	1 654.74	16.33	−5.545	7.519	13.064	0.000 97	0.022 7	1 036.4	44.053
255.37	0	1 951.22	19.26	−5.054	7.530	12.584	0.000 99	0.018 9	1 010.8	52.910
260.93	10	2 309.74	22.80	−4.583	7.540	12.123	0.001 02	0.016 4	980.3	60.976
266.48	20	2 688.27	26.33	−4.072	7.530	11.602	0.001 06	0.013 5	948.3	74.074
273.15	32	3 171.59	31.30	−3.407	7.519	10.926	0.001 10	0.011 1	913.1	90.090
277.59	40	3 585.27	35.38	−2.885	7.499	10.384	0.001 14	0.010 0	876.2	100.00
283.15	50	4 067.91	40.15	−2.159	7.427	9.586	0.001 19	0.008 6	837.8	116.28
288.71	60	4 653.96	45.93	−1.453	7.366	8.819	0.001 27	0.007 4	788.1	135.14
294.26	70	5 240.02	51.71	−0.716	7.233	7.949	0.001 34	0.006 6	744.9	151.52
299.82	80	5 963.96	58.86	0.000	7.059	7.059	0.001 56	0.005 0	640.7	200.00
309.26	97	7 370.49	72.74	6.803	6.803	0.000	0.002 35	0.002 35	424.5	424.50

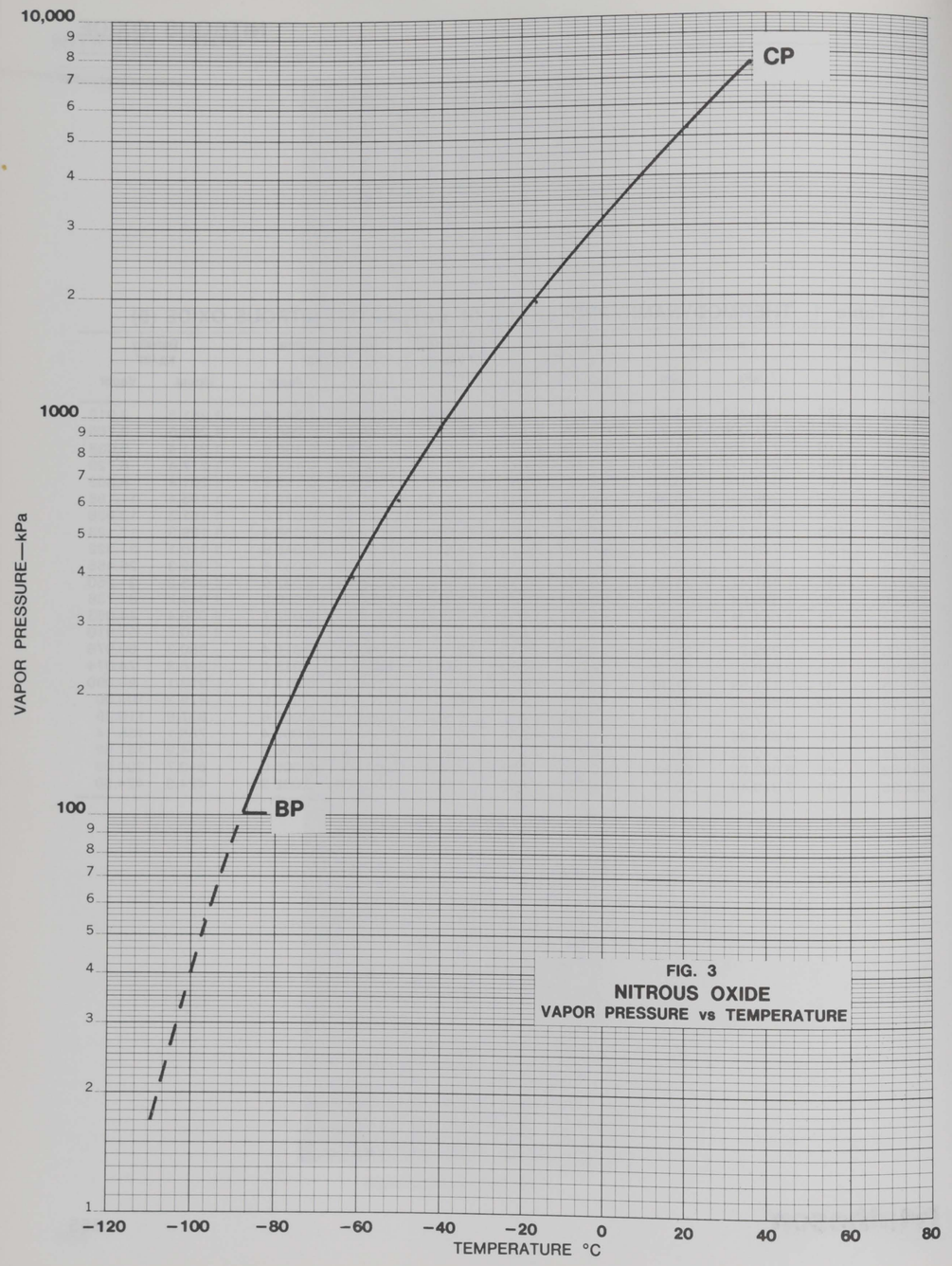


FIG. 3
NITROUS OXIDE
VAPOR PRESSURE vs TEMPERATURE

OCTAFLUOROCYCLOBUTANE

(Synonyms: Perfluorocyclobutane; Freon-C318®)
(Formula: C_4F_8 or $CF_2 \cdot CF_2 \cdot CF_2 \cdot CF_2$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.200 031 kg
One Mole of C_4F_8	0.200 031 kg
Specific Volume @ 21.1 °C, 101.325 kPa	115.5 dm^3/kg; 1.85 ft^3/lb
Vapor Pressure @ 21.1 °C	274 kPa; 2.74 bar; 39.7 psia; 2.7 atm
Boiling Point @ 101.325 kPa	267.30 °K; −5.8 °C; 21.5 °F
Triple Point	
Temperature	232.95 °K; −40.2 °C; −40.4 °F
Pressure	19.04 kPa; 190.4 mbar; 142.8 mmHg
Absolute Density, Gas @ 101.325 kPa @ 21.1 °C	8.66 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 21.1 °C	7.33
Density, Liquid @ Saturation Pressure @ 21.1 °C	1.513 kg/l
Critical Temperature	388.45 °K; 115.3 °C; 239.5 °F
Critical Pressure	2 786 kPa; 27.86 bar; 404.1 psia; 27.5 atm
Critical Volume	1.615 dm^3/kg
Critical Density	0.619 kg/dm^3
Critical Compressibility Factor	0.279
Latent Heat of Fusion @ −40.2 °C	2 766.88 J/mol; 661.3 cal/mol
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	159.017 J/(mol·°K)
@ Constant Volume	150.727 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.055
Molar Specific Heat, Liquid @ −27.1 °C	202.28 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.012 mPa·s; 0.012 cP
Viscosity, Liquid At Saturation Pressure @ 25 °C	0.42 mPa·s; 0.42 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.010 20 W/(m·°K); 24.4 × 10^{-6} cal·cm/s·cm^2·°C)
Thermal Conductivity, Liquid At Saturation Pressure @ 25 °C	0.043 2 W/(m·°K); 103.3 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 21.1 °C	8.3 mN/m; 8.3 dyn/cm
Solubility In Water @ 101.325 kPa @ 21.1 °C	0.014% (by weight)
Dielectric Constant, Gas @ 51 kPa @ 10 °C	1.003 4
Refractive Index, Liquid, n_D @ 25 °C	1.217
Relative Dielectric Strength (Nitrogen = 1)	2.86

Description

At room temperature and atmospheric pressure, octafluorocyclobutane is a nonflammable, colorless, odorless, and tasteless gas. It is shipped as a liquefied gas under its own vapor pressure of 170 kPa (25 psig) at 21.1 °C.

Specifications

Octafluorocyclobutane has a minimum purity of 99.9 mole %.

Uses

Octafluorocyclobutane is of interest as a gaseous dielectric, as a foam producing agent, and as a propellant.

Toxicity

Octafluorocyclobutane has been tested on a very preliminary basis. This work indicates that the compound is probably nontoxic, but adequate ventilation should be used in any experimental work until further toxicity information becomes avail-

able. Inhalation of octafluorocyclobutane that has been exposed to flame temperatures should be avoided, since under some conditions it may decompose slightly and form toxic or irritating decomposition products.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Leak Detection

All fittings and joints should be painted with soap solution to detect leaks, which will be indicated by bubble formation.

Disposal of Leaking Cylinders

For disposal procedure see Appendx II-C.

Materials of Construction

Cast iron and stainless steel are satisfactory up to a temperature of 120 °C. Steel is satisfactory up to temperatures of 175 °C. At 400 °C Inconel, nickel, and platinum show only slight deterioration. At temperatures of about 500 °C, these metals will act as catalysts, to varying degrees, for the decomposition of octafluorocyclobutane.

Cylinder and Valve Description

Octafluorocyclobutane is shipped in DOT approved low pressure steel cylinders. Cylinders of octafluorocyclobutane are equipped with the approved alternate Compressed Gas Association (CGA) valve outlet connection No. 660. The valve outlet has a thread size of 1.030 inches diameter, right-hand external threads, with a flat seat using a washer to seal (See Figure 1).

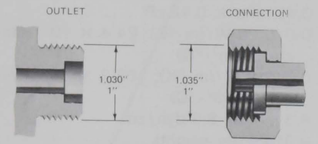


Fig. 1 CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

Lecture bottles have a special 5/16 inch-32 threads per inch female, valve outlet and a 9/16 inch-18 threads per inch male, dual valve outlet.

Safety Devices

Cylinders of octafluorocyclobutane contain, as safety devices, fusible metal plugs, melting at about 73.9 °C (165 °F). These devices are usually an integral part of the cylinder valve.

Recommended Controls

Automatic Pressure Regulators

For automatic regulation of octafluorocyclobutane, Matheson has available regulator Model 1P-660. This regulator has a brass body, neoprene rubber diaphragm, and neoprene seat. It has a delivery pressure range of 28–240 kPa (4–35 psig). No cylinder pressure gauge is provided, since it would not indicate cylinder content but only vapor pressure which will remain constant as long as liquid remains in the cylinder.

For accurate low pressure control, Matheson supplies a Model 70 low pressure regulator, which has an oversize, pancake body of die cast aluminum and a Buna N diaphragm. Three pressure ranges are available as follows:

Model No.	Delivery Pressure Range kPa	mbar (g)	psig
70B-660	0.5–3.0	5–30	2–12 inches water column
70-660	3.4–34.5	34–345	0.5–5.0 psig
70A-660	34.5–68.9	345–689	5–10 psig

Manual Controls

Needle valve Model 50-660, of chrome plated brass bar stock, is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a connection hose, ¼" tube fitting, or ¼" NPT male or female pipe. It should be used only for intermittent flow control. It should not be used as a pressure control, since dangerous pressures can develop if a line or system becomes clogged. Needle valve Model 31B is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Octafluorocyclobutane is classified by the DOT as a nonflammable, compressed gas and is shipped with the required "Green Label".

Chemical Preparation

Octafluorocyclobutane is obtained by the dimerization of tetrafluoroethylene at elevated temperatures.

Chemical Properties

Octafluorocyclobutane is extremely stable. It is unreactive with other materials under ordinary conditions. At high temperatures (600 °C), it dissociates to form carbon and carbon tetrafluoride, and some toxic compounds. Metals catalyze the decomposition of octafluorocyclobutane at elevated temperatures.

Thermodynamic and Detailed Physical Data

Molecular Structure (2)

High-resolution infrared spectra indicate that octafluorocyclobutane is a puckered ring, of D_{2d} symmetry, and that is not a planar ring of D_{4d} symmetry. The C—C and C—F bond distances are 1.53 Å (1.53×10^{-10} m) and 1.36 Å (1.36×10^{-10} m), respectively. The C—C—C and F—C—F bond angles are 90° and 112°, respectively.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous octafluorocyclobutane.

Vapor Pressure (3)

The vapor pressure of liquid octafluorocyclobutane up to 101.325 kPa is shown below:

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
177.35	0.653	6.53	4.9
191.8[1]	1.093	10.9	8.2
196.85	1.453	14.5	10.9
197.16	1.467	14.7	11.0
206.69	2.893	28.9	21.7
213.08	4.786	47.9	35.9
221.59	9.026	90.3	67.7
230.80	16.759	168	125.7
241.31	30.171	302	226.3
253.00	54.195	542	406.5
259.50	72.967	730	547.3
263.87	88.246	882	661.9
267.16	99.152	992	743.7
267.30	101.325	1 013.25	760.0

The vapor pressure of liquid octafluorocyclobutane above 101.325 kPa up to the critical point is shown below:

Temperature, °K	Vapor Pressure kPa	bar	atm
267.16	101.325	1.013 25	1.000
303.15	365.479	3.65	3.607
323.15	647.872	6.48	6.394
348.15	1 200.904	12.0	11.852
373.15	2.053.858	20.5	20.270
387.65	2 738.105	27.4	27.023
388.37	2 777.521	27.8	27.412

See Figure 3 for vapor pressure curve.

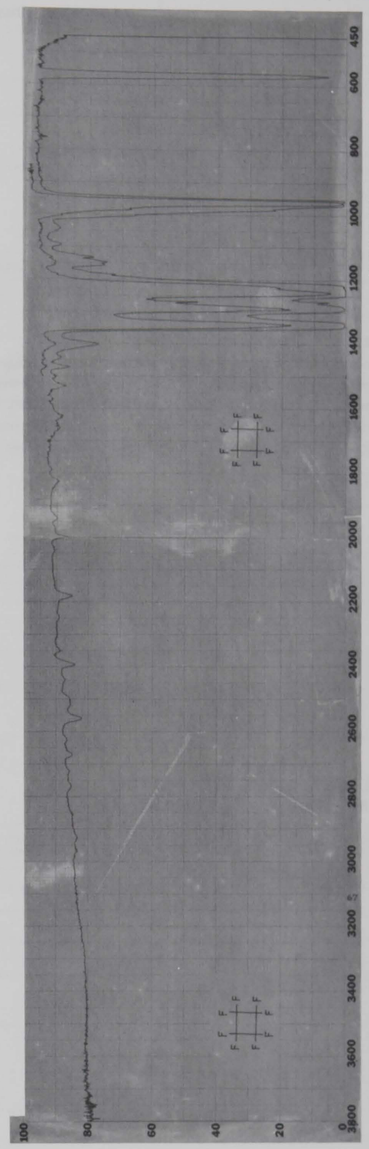


Fig. 2. Infrared spectrum of gaseous octafluorocyclobutane; 10-cm path length cell, with KBr windows; cell pressure: curve A (complete scan): 2.666 kPa (20 mmHg); curve B (partial scan): 0.067 kPa (0.5 mmHg) (4).

OCTAFLUOROCYCLOBUTANE

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/kg
@ 261.24	118.54; 28.33 kcal/kg
@ 267.30	116.19; 27.77 kcal/kg
@ 294.26	106.92; 25.56 kcal/kg

Thermodynamic Data

Entropy, Ideal Gas @ 261.24 °K	380.52 J/(mol·°K); 90.95 cal/mol·°K)

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of octafluorocyclobutane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] R. P. Bauman and B. J. Bulkin, *J. Chem. Phys.* 45, 496–498 (1966).

[3] *"Freon"—C 318, Tech. Bull.* B—18B, *1958*, E.I. duPont de Nemours & Co., Inc., Wilmington, Delaware.

[4] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Matheson

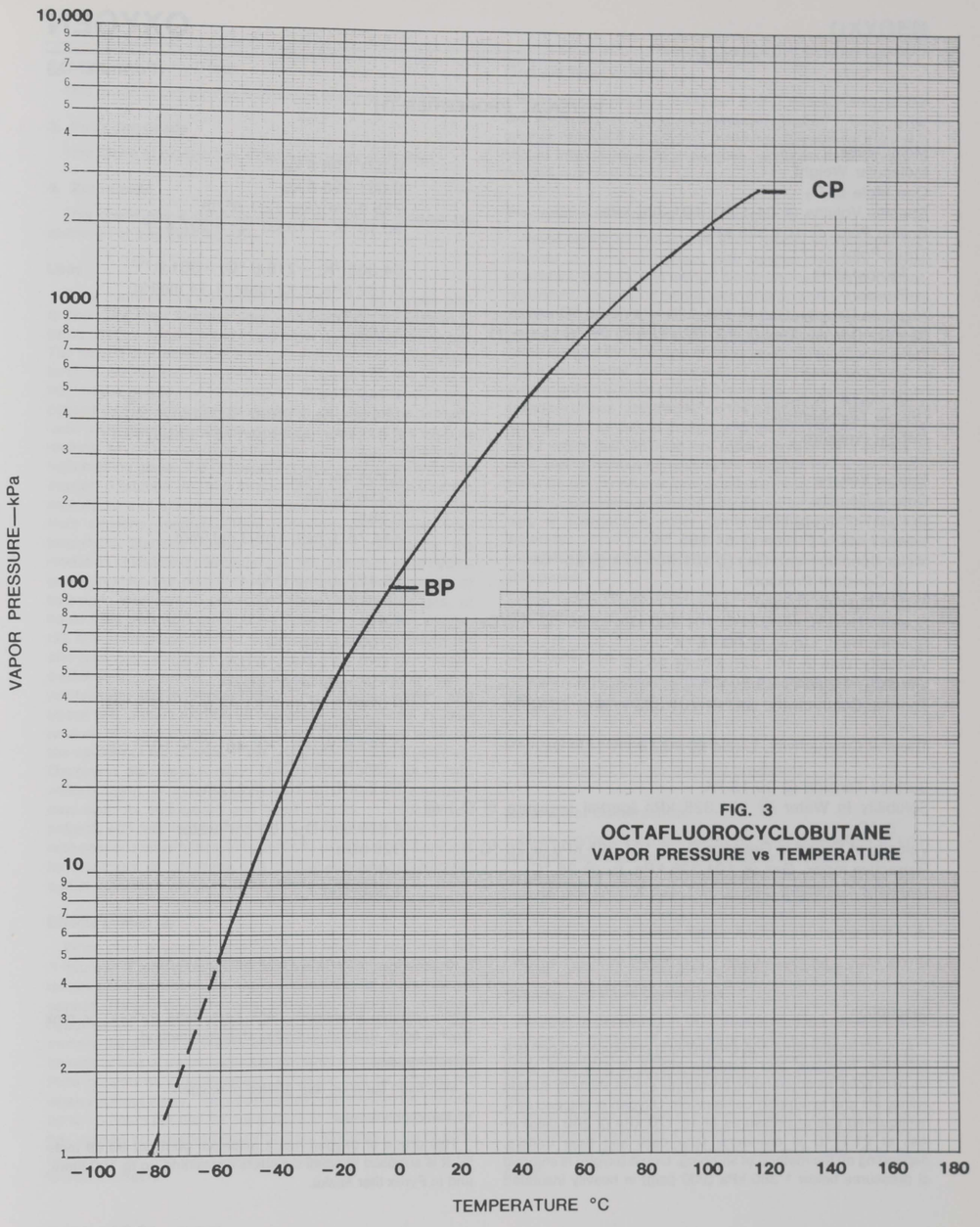


FIG. 3
OCTAFLUOROCYCLOBUTANE
VAPOR PRESSURE vs TEMPERATURE

OXYGEN

(Formula: O_2)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.031 998 8 kg
One Mole of O_2	0.031 998 8 kg
Specific Volume @ 21.1 °C, 101.325 kPa	755.4 dm^3/kg; 12.1 ft^3/lb
Boiling Point @ 101.325 kPa	90.18 °K; −183.0 °C; −297.4 °F
Triple Point	
Temperature	54.363 °K; −218.8 °C; −361.8 °F
Pressure	0.152 kPa; 1.52 mbar; 1.14 mmHg
Absolute Density, Gas @ 101.325 kPa @ 25 °C	1.309 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.105
Density, Liquid	
@ 54.363 °K	1.321 5 kg/l
@ 90.18 °K	1.140 7 kg/l
Critical Temperature	154.58 °K; −118.6 °C; −181.4 °F
Critical Pressure	5 043 kPa; 50.43 bar; 731.4 psia; 49.77 atm
Critical Volume	2.294 dm^3/kg
Critical Density	0.436 kg/dm^3
Critical Compressibility	0.288
Latent Heat of Fusion @ 54.363 °K	444.76 J/mol; 106.3 cal/mol
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	29.427 J/(mol·°K)
@ Constant Volume	20.817 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.414
Specific Heat, Liquid @ 90.18 °K	1.703 kJ/(kg·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.020 75 mPa·s; 0.020 75 cP
Viscosity, Liquid @ 99.70 °K	0.156 mPa·s; 0.156 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25°C	0.0266 2 W/(m·°K) 63.6 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ 90.18 °K	0.192 9 W/(m·°K); 461.0 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 90.15 °K	13.2 mN·m; 13.2 dyn/cm
Solubility In Water @ 101.325 kPa (partial pressure of O_2) @ 0 °C	4.889 cm^3 O_2/100 cm^3 water
Velocity of Sound In Gaseous O_2 @ 101.325 kPa @ 20 °C	326 m/s
Refractive Index, Gas @ 101.325 kPa, n_D @ 25 °C	1.000 271 2
Dielectric Constant, Gas @ 101.325 kPa @ 20 °C	1.000 494 7

Description

At room temperature and atmospheric pressure, oxygen is a colorless, odorless, and tasteless gas. It is pale blue when liquid or solid. Its outstanding properties are its ability to sustain animal life and to support combustion. Oxygen is shipped as a nonliquefied gas at pressures of 15 170 kPa (2 200 psig) or less at 21.1 °C in clyinders, tank cars and tube trailers, depending on the method of shipping. Liquid oxygen is shipped at pressures below 1 380 kPa (200 psig) in heavily insulated small portable containers, tank cars, tube trailers, or tank trucks, again depending on the shipping method.

Specifications

Matheson supplies four grades of oxygen.

1. Research Grade

This grade of oxygen has a minimum purity of 99.99 mole %. It is supplied in small cylinders containing up to 100 liters, and in Pyrex liter flasks.

2. Ultra High Purity Grade

This grade of oxygen has a minimum purity of 99.99%.

3. Extra Dry Grade

This grade of oxygen has a minimum purity of 99.6%.

4. Zero Grade

This grade has a certified total hydrocarbons content (as methane) of less than 0.5 ppm.

Uses

Steel manufacture consumes over 60% of all oxygen produced. The steel industry uses vast quantities of oxygen in basic oxygen furnaces and in the older open hearth furnaces. The cutting and welding of ferrous metals by the oxyacetylene torch is carried out on a large scale. Oxygen is also used in nonferrous metallurgy, primarily to increase combustion processes by supplementing or replacing air. Oxygen is similarly used in the glass industry for a variety of applications such as melting, severing, polishing and glass blowing of ordinary and high-melting glass. The chemical industry used over 15% of all oxygen produced in 1978 in such diverse operations as the manufacture of acetylene from hydrocarbons, ethylene oxide from ethylene, methanol from hydrocarbons, acrolein from propylene, titanium dioxide from titanium tetrachloride, the oxidation of liquefied petroleum gas, the manufacture of hydrogen peroxide, the manufacture of synthesis gas (mixture of hydrogen and carbon monoxide) from coal, natural gas, or liquid fuels synthesis gas is used to produce gasoline, methanol, and ammonia and in the Oxo process to produce aldehydes and alcohols), and the manufacture of nitric acid by catalytic oxidation of ammonia. Oxygen is finding increasing use in waste-water quality improvement. Fuel cells for military and space use contain oxygen as one of the components. A large amount of liquid oxygen is consumed in aerospace uses, as the oxidant of liquid fuels in the propulsion of space vehicles. Oxygen is also used in such diverse applications as in high altitude flying, in underwater operations, in first aid emergencies such as suffocation and heart attacks, in treatment of patients with respiratory disorders, in anesthesia in conjunction with gaseous anesthetics, in hyperbaric oxygenation chambers for treatment of gangrene and carbon monoxide poisoning, and in admixture with helium in asthmatic attacks.

Effects in Man (2)

When pure oxygen is breathed for 5 hours at sea level, for 3 hours at 3 atmospheres, 30 minutes at 4 atmospheres, or 5 minutes at 7 atmospheres, signs and symptoms of toxicity will appear. These include nausea, dizziness, bronchial irritation, hypothermia, increased depth of respiration, bradycardia, pulmonary discomfort or injury, peripheral vasoconstriction, amblyopia or loss of vision, syncope, epileptic seizures, and death. Pure oxygen at ⅓ atmospheric pressure can be inhaled for weeks without injury. The inhalation of pure oxygen for periods up to 16 hours per day for many days at atmospheric pressure has caused no observed injury to man. Mixtures of up to 65% oxygen in air may be inhaled for extended periods with no known ill effects.

First Aid Treatment (2)

In cases of exposure to oxygen at 3–7 atmospheres, all but the most severe cases (pneumonia) recover rapidly after prompt reduction of oxygen pressure. Supportive treatment should include immediate sedation, anticonvulsive therapy if needed, and rest.

Precautions in Handling and Storage

Never permit oil, grease, or other readily combustible substances to come in contact with oxygen cylinders, valves, regulators, gauges, and fittings. Never lubricate oxygen valves, regulators, gauges, or fittings with oil or any other combustible substance. In welding shops and industrial plants using both oxyacetylene and electric welding apparatus, care should be taken to avoid the handling of these equipments in any manner which may permit the compressed gas cylinders to come in contact with electrical circuits. Never use manifolds for oxygen cylinders unless constructed on the advice of a qualified engineer. Manifolds should comply with the standards of a recognized safety authority. Do not supply oxygen by a system of shop piping without consulting the supplier for recommendations. Do not permit any foreign substance to enter the cylinder or valve. Cylinders of oxygen should not be stored near cylinders of acetylene or other combustible gases. Unless well separated, there should be a fire-resistant partition between oxygen cylinders and acetylene, or other cylinders of combustible gases.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Lines and equipment to contain oxygen should be pretested with an inert gas, such as nitrogen.

Disposal of Leaking Cylinders

See Appendix II-C for disposal procedure.

Materials of Construction

Since oxygen is noncorrosive, no special materials of construction are required. However, extreme caution should be taken to avoid contact with oil, grease, or other readily combustible substances in piping or vessels. The system should be designed to have a working pressure as specified by competent engineers, using a safety factor conforming to the A.S.M.E. code for pressure piping.

Cylinder and Valve Description

Oxygen is packaged in DOT approved, high pressure steel cylinders. Cylinders of oxygen are equipped with brass valves with valve outlet connection No. 540, designated as standard by the Compressed Gas Association (CGA). The valve outlet has a thread size of 0.903 inch diameter, with right-hand external threads accepting a round shaped nipple (see Figure 1). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet and a 9/16-18 threads per inch male, dual valve outlet.

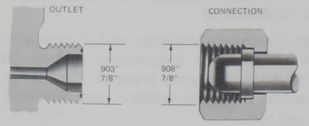


Fig. 1. CONNECTION 540 .903"-14 RH EXT. accepting a Round Shaped Nipple

Safety Devices

Cylinders containing oxygen have safety devices of either the frangible disc type or frangible disc type backed up with fusible metal, melting at approximately 100 °C (212 °F). Cylinders pressurized 10% in excess of their marked service pressure in accordance with present DOT regulations must be equipped only with safety devices of the unbacked frangible disc type. These safety devices are usually an integral part of the cylinder valve, situated opposite the valve outlet.

Recommended Controls

In order to reduce the high cylinder pressure of oxygen to a safe working value consistent with a system's design, the following types of controls are recommended.

Automatic Pressure Regulators

1. Single Stage Regulators

A single stage regulator will reduce cylinder pressure in one stage to a delivery pressure in a particular range depending upon the design of the regulator and its spring load. A single stage regulator will show a slight variation in delivery pressure as cylinder pressure falls. The following single stage regulators are available from Matheson for Extra Dry Grade oxygen:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
1L-540	28–550	0.28–5.5	4–80
1H-540	69–1 240	0.69–12.4	10–180
2-540	345–4 480	3.45–44.8	50–650
3-540	690–10 340	6.9–103.4	100–1 500
4-540	690–17 240	6.9–172.4	100–2 500
3320 (for lecture bottles)	28–410	0.28–4.1	4–60

Single stage regulators Model 19-540 and Model 3 500-540 with delivery pressure ranges of 28–345 kPa (4–50 psig) and 28–520 kPa (4–75 psig), respectively, are recommended for use with Research Grade and Ultra High Purity Grade oxygen.

The Model 19-540 regulator is of all brass construction with a German silver alloy diaphragm with nylon seat and aluminum and nylon gaskets. The regulator is an ideal instrument for normal laboratory use of high purity gases, or where diffusion of air would be deleterious. The regulator can be supplied with a helium leak rate certification if desired, the maximum acceptable leak rate being 2×10^{-9} cm^3. It is provided with a diaphragm packless outlet valve with ¼" Gyrolok tube fitting. It has two 2½" gauges, a delivery pressure gauge of 0–690 kPa (0–100 psig) and a cylinder pressure gauge of 0–20 680 kPa (0–3 000 psig).

The Model 3500-540 stainless steel regulator has a cylinder pressure gauge and a delivery pressure gauge. All parts in the gas stream are type 316 stainless steel. It has a type 301 stainless steel diaphragm, a Tefzel seat, and Teflon gaskets. The regulator can be supplied with a helium leak rate certification, the maximum acceptable leak rate being 2×10^{-10} cm^3. It is provided with a diaphragm packless outlet valve with ¼" Gyrolok tube fitting.

2. Two Stage Regulators

This type of regulator performs the same function as single stage regulators. However, greater accuracy and control of delivery pressure is maintained, and the delivery pressure does not vary as cylinder pressure falls. The following two stage regulators are available from Matheson for Extra Dry Grade oxygen:

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
8L-540	14-104	0.14–1.04	2–15
8-540	28–345	0.28–3.45	4–50
8H-540	69–690	0.69–6.9	10–100
9-540	138–1 720	1.38–17.2	20–250

Two stage stainless steel regulator Model 3800-540 and two stage metal diaphragm brass regulator Model 3104-540 with delivery pressure ranges of 28–620 kPa (4–90 psig) and 28–690 kPa (4–100 psig), respectively, are recommended for use with Research Purity, Ultra High Purity, and Zero Grades of oxygen.

3. Low Pressure Regulator

The above regulators are not satisfactory for accurate delivery pressures below 3.4 kPa (5 psig). Therefore, an auxilary regulator specifically designed for low pressures is recommended to be used in series with any of the standard regulators having maximum delivery pressures up to 1 720 kPa (250 psig). Matheson has various models known as the Model 70 regulator which may be obtained with delivery pressures ranging from 2 inches water column to 69 kPa (10 psig), as follows:

Model No.	Delivery Pressure Range		
	kPa	mbar (g)	psig
70B	0.5–3.0	5–30	2–12 inches water column
70	3.4–34.5	34–345	0.5–5.0 psig
70A	34.5–68.9	345–689	5–10 psig

When this regulator is used in conjunction with a standard regulator, an extra heavy hose is available to connect to the standard regulator. All Matheson regulators are provided with needle valves so that accurate flow control can be maintained.

Manual Controls

Manual needle valves for direct attachment to the cylinder valve outlet are available. These types of controls are used mainly where intermittent flows are necessary, or where it is desired to control the flow of gas directly from the cylinder. This type of a needle valve will allow control of extemely small flow rates on up to relatively large flow rates. However, pressures cannot be controlled with such a valve and, if a line or system becomes plugged, dangerous pressures can build up. The following manual type valves are recommended for use with oxygen: Model 50–540 and Model 52–540 with tank gauge. These values are supplied with hose connections, ¼" tube fittings, or ¼" NPT male or female outlets. Needle valve Model 31B or 30AR is recommended for use with lecture bottles.

Needle valve Model 4351–540 is recommended for use with Research Purity and Ultra High Purity Grades of oxygen.

Flowmeters

Matheson Series 7600 laboratory brass or stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass or stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Oxygen is shipped in high pressure steel cylinders as a nonflammable compressed gas, taking a DOT "Green Label." They are usually filled to the marked service pressure of the cylinder or to a maximum of 10% in excess of the marked service pressure in accordance with present DOT regulations.

Commercial Preparation

Oxygen is obtained on a commercial scale from the liquefaction of air, the pure substance being separated from the other components by distillation. Some oxygen is obtained by the electrolysis of water.

Chemical Properties

Oxygen combines directly with all other elements except the rare gases, usually producing an oxide. Its reactivity, however, varies widely in these cases. Some elements, alkali or alkaline earth metals, ignite spontaneously, but most of the elements do not oxidize rapidly at ordinary temperatures. Thus, carbon must be heated before ignition and the noble metals are oxidized only at very high temperatures. Energy for heat, light, and power is produced by the combustion of hydrocarbons, such as petroleum, coal, and natural gas. When these materials are burned in an excess of air at temperatures below 1 131 °C, the products formed are carbon dioxide, water, nitrogen, and unreacted oxygen. At temperatures above 3 000 °F and with less than the required amount of oxygen, hydrogen and carbon monoxide are also formed. At lower temperatures, oxygen reacts with organic compounds, e.g., phenol is obtained from benzene, phthalic anhydride from naphthalene, etc., and a variety of alcohols, aldehydes, acids, and ketones from alkanes. Oxygen can be converted to ozone in low yield by subjecting it to a silent electric discharge.

Thermodynamic and Detailed Physical Data

Molecular Structure

The linear oxygen molecule has $D_{\infty h}$ point group symmetry and a symmetry number of two. The O—O bond distance is 1.207 4 Å ($1.207\ 4 \times 10^{-10}$ m).

The oxygen molecule is paramagnetic and is best described by the canonical forms $\dot{O}:\ :\dot{O}$ and $:O:::O:$

Infrared Spectrum

The homopolar oxygen molecule is not infrared active.

Vapor Pressure (3)

The vapor pressure of liquid oxygen is represented by the following Antoine vapor pressure equation:

$$\log_{10} p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.691 44, 319.013, and 266.697, respectively.

Some calculated vapor pressure values are shown below:

Temperature, °K	Vapor Pressure		
	kPa	mbar	mmHg
62.50	1.332	13.3	10
65.63	2.666	26.7	20
69.14	5.333	53.3	40
71.38	7.999	80.0	60
73.08	10.666	107	80
74.45	13.332	133	100
79.11	26.664	267	200
82.15	39.997	400	300
84.46	53.329	533	400
86.36	66.661	667	500
87.97	79.993	800	600
89.39	93.325	933	700
90.17	101.325	1 013.25	760
90.66	106.658	1 067	800
91.81	119.990	1 200	900
92.87	133.322	1 333	1 000

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
94.77	159.986	1 600	1 200
97.20	199.983	2 000	1 500

For additional vapor pressure data, see Table 2.

Latent Heat of Vaporization, ΔHv (3) @ 90.17 K 6 819.92 J/mol; 1 630 cal/mol

For additional ΔHv values, see Table 2.

For density data on gaseous oxygen at various temperatures and pressures, see Table 1.

Thermodynamic Data

Thermodynamic properties of saturated oxygen and superheated oxygen are shown in Tables 2 and 3. For compressibility data, see Table 4.

Thermodynamic Properties of Oxygen As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	29.372 J/(mol·°K)
Entropy, S°	205.033 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−205.033 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	9.682 kJ/mol
Enthalpy of Formation ΔH_f°	0.000 kJ/mol
Free Energy of Formation, ΔF_f°	0.000 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of oxygen, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatments*, 2nd edition, *1977* pp. 123-125, Matheson, Lyndhurst, New Jersey.

[3] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds*, *1968*, Volume 1, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[4] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D.C.

[5] *Compressed Gas Handbook*, J. S. Kunkle, S. D. Wilson, and R. A. Cota, editors, *1969*, p. 554, NASA SP-3045, U. S. Government Printing Office, Washington, D.C.

[6] J. Hilsenrath, *et al.*, *Tables of Thermal Properties of Gases*, *1955*, pp. 394-399, Natl. Bur. Stand. Circ. 564, U. S. Government Printing Office, Washington, D.C.

[7] *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p. 3-183, McGraw-Hill Book Co., inc., New York, New York.

[8] See reference 6, pp. 406-411.

[9] See reference 6, pp. 412-417.

[10] See reference 7, p. 3-108.

Table 1. DENSITY OF GASEOUS OXYGEN (6)

UNIT: kg/m³

Temperature, °K	Pressure, kPa 101.325	405.300	709.275	1 013.250	4 053.000	7 092.750	10 132.500
180	2.176	8.814	15.630	22.635	106.60	235.64	
210	1.862	7.505	13.238	19.061	83.02	159.05	24.07
240	1.627	6.541	11.503	16.512	69.39	127.18	188.49
270	1.446	5.800	10.181	14.587	60.09	107.925	157.15
300	1.301	5.212	9.138	13.077	53.203	94.431	136.24
330	1.182	4.733	8.292	11.856	47.850	84.307	120.92
360	1.083	4.336	7.591	10.848	43.542	76.331	109.046
400	0.975	3.900	6.284	9.747	38.935	67.959	96.729
450	0.866	3.464	6.060	8.653	34.439	59.919	85.044
500	0.780	3.117	5.451	7.782	30.906	53.668	76.047
550	0.709	2.833	4.954	7.072	28.050	48.659	68.885
600	0.650	2.597	4.540	6.481	25.689	44.535	63.016
650	0.600	2.397	4.191	5.981	23.701	41.077	58.113
700	0.557	2.226	3.891	5.554	22.004	38.131	53.940
750	0.520	2.077	3.632	5.183	20.536	35.592	50.349
800	0.487	1.947	3.405	4.859	19.255	33.374	47.221
900	0.433	1.731	3.028	4.320	17.123	29.689	42.018
1 000	0.390	1.558	2.724	3.888	15.419	26.747	37.876
1 500	0.260	1.039	1.817	2.594	10.308	17.918	25.428
2 000	0.195	0.779	1.363	1.947	7.745	13.484	19.163

Table 2. THERMODYNAMIC PROPERTIES OF SATURATED OXYGEN (7)

Temperature °K	Temperature °F	Pressure kPa	Pressure atm	Entropy J/(mol·°K) Liquid	Entropy J/(mol·°K) Vapor	Enthalpy J/mol Liquid	Enthalpy J/mol Vapor	Latent Heat of Vaporization J/mol	Specific Volume dm³/kg Liquid	Specific Volume dm³/kg Vapor	Density kg/dm³ Liquid	Density kg/dm³ Vapor
70	−333.7	6.181	0.061	80.39	185.9	−5 362	2 022	7 384	0.809 8	2.921	1.235	0.000 342
80	−315.7	30.094	0.297	87.33	176.5	−4 841	2 295	7 136	0.841 0	682.4	1.189	0.001 47
90	−297.7	99.400	0.981	93.88	169.7	−4 288	2 542	6 830	0.876 1	227.8	1.141	0.004 39
90.18	−297.3	101.325	1.000	93.94	169.6	−4 278	2 548	6 826	0.876 6	223.7	1.141	0.004 47
100	−279.7	254.224	2.509	99.74	164.5	−3 723	2 755	6 478	0.917 0	95.83	1.091	0.010 44
110	−261.7	543.406	5.363	105.1	160.2	−3 149	2 913	6 062	0.966 3	46.99	1.035	0.021 28
120	−243.7	1 021.56	10.082	110.2	156.5	−2 555	3 001	5 556	1.027 7	25.47	0.973	0.039 26
130	−225.7	1 747.75	17.249	115.1	152.8	−1 913	2 992	4 905	1.109 4	14.64	0.901	0.068 29
140	−207.7	2 786.44	27.50	120.2	148.9	−1 180	2 834	4 014	1.231 3	8.578	0.812	0.116 57
150	−189.7	4 219.17	41.64	126.4	143.5	−228.9	2 338	2 566.9	1.478 3	4.683	0.676	0.213 53
154.77	−181.1	5 080.44	50.14	134.9	134.9	1 123	1 123	0	2.344 4	2.344 4	0.426 54	0.426 54

Table 3. THERMODYNAMIC PROPERTIES OF SUPERHEATED OXYGEN, H, ENTHALPY, J/mol (8); S, ENTROPY, J/(mol • °K) (9); V, SPECIFIC VOLUME, dm^3/kg (6)

Pressure kPa	atm		180	210	240	270	300	330	360	400	450
101.325	1	H	5 211.0	6 089.0	6 966.6	7 845.5	8 726.7	9 612.0	10 503	11 702	13 220
		S	190.263	194.774	198.680	202.130	205.224	208.037	210.621	213.778	217.354
		V	459.6	537.1	614.6	691.6	768.6	846.0	923.4	1 026	1 155
405.300	4	H	5 153.0	6 044.2	6 930.9	7 816.2	8 702.9	9 592.0	10 486	11 688	13 210
		S	178.519	183.099	187.045	190.521	193.634	196.460	199.053	202.219	205.802
		V	113.5	133.2	152.9	172.4	191.9	211.3	230.6	256.4	288.7
709.275	7	H	5 093.5	5 998.8	6 895.0	7 787.1	8 678.8	9 572.3	10 470	11 675	13 200
		S	173.642	178.295	182.282	185.785	188.916	191.755	194.358	197.532	201.125
		V	63.98	75.54	86.93	98.22	109.4	120.6	131.7	159.1	165.0
1 013.250	10	H	5 032.9	5 952.9	6 858.7	7 758.1	8 654.9	9 552.3	10 453	11 662	13 190
		S	170.446	175.175	179.206	182.737	185.886	188.737	191.350	194.533	198.133
		V	44.18	52.46	60.56	68.55	76.47	84.35	92.18	102.6	115.6
4 053.000	40	H	4 326.6	5 464.4	6 475.1	7 463.0	8 414.7	9 354.9	10 288	11 533	13 096
		S	156.122	161.977	166.530	170.361	173.705	176.689	179.399	182.676	186.356
		V	9.381	12.05	14.41	16.64	18.80	20.90	22.97	25.68	29.04
7 092.750	70	H	3 384.0	4 928.4	6 107.2	7 170.1	8 180.7	9 161.9	10 129	11 408	13 002
		S	147.492	155.424	160.686	164.860	168.406	171.526	174.331	177.700	181.456
		V	4.244	6.287	7.863	9.266	10.59	11.86	13.10	14.71	16.69
10 132.500	100	H		4 351.5	5 737.0	6 893.0	7 960.4	8 980.2	9 979.5	11 290	12 916
		S		150.352	156.538	161.086	164.827	168.078	170.968	174.442	178.250
		V		4.047	5.305	6.363	7.340	8.270	9.170	10.34	11.76

Temperature, °K 500	550	600	650	700	750	800	900	1 000	1 500	2 000
14 763	16 331	17 924	19 540	21 180	22 839	24 517	27 924	31 387	49 290	67 881
220.604	223.593	226.364	228.953	231.380	233.671	235.837	239.848	243.497	257.992	268.679
1 282	1 410	1 538	1 667	1 795	1 923	2 053	2 309	2 564	3 846	5 128
14 755	16 325	17 920	19 538	21 179	22 839	24 519	27 926	31 390	49 297	67 888
209.058	212.050	214.825	217.416	219.845	222.138	224.304	228.317	231.967	246.465	257.152
320.8	353.0	385.1	417.2	449.2	481.5	513.6	577.7	641.8	962.5	1 284
14 748	16 320	17 917	19 536	21 177	22 839	24.519	27 928	31 394	49 303	67 896
204.385	207.382	210.159	212.753	215.185	217.477	219.646	223.660	227.311	241.811	252.500
183.5	201.9	220.3	238.6	257.0	275.3	293.7	330.3	367.1	550.4	733.7
14 741	16 315	17 913	19 534	21 177	22 839	24 521	27 931	31 397	49 309	67 904
201.400	204.400	207.181	209.776	212.210	214.504	216.674	220.689	224.342	238.844	249.533
128.5	141.4	154.3	167.2	180.1	192.9	205.8	231.5	257.2	385.5	513.6
14 672	16 266	17 881	19 516	21 170	22 843	24 533	27 956	31 433	49 375	67 983
189.677	192.717	195.528	198.145	200.596	202.903	205.084	209.117	212.779	227.306	238.003
32.36	35.65	38.93	42.19	45.45	48.69	51.93	58.40	64.86	97.01	129.1
14 606	16 221	17 851	19 500	21 165	22 848	24.544	27 983	31 472	49 441	68 062
184.831	187.910	190.749	193.388	195.856	198.177	200.369	204.418	208.091	222.643	233.347
18.63	20.55	22.45	24.34	26.23	28.10	29.96	33.68	37.39	55.81	74.16
14 542	16 175	17 824	19 484	21 163	22 855	24 560	28 010	31 510	49 509	68 142
181.677	184.793	187.659	190.320	192.804	195.138	197.341	201.406	205.090	219.666	230.379
13.15	14.52	15.87	17.21	18.54	19.86	21.18	23.80	26.40	39.33	52.18

Table 4. COMPRESSIBILITY FACTORS, Z = PV/RT, FOR OXYGEN (10)

Temperature, °K	Pressure, kPa 100	500	1 000	2 000	4 000	6 000	8 000	10 000	20 000	30 000	40 000	50 000
75	0.004 3	0.021 3	0.042 5	0.084 9	0.169 3	0.253 3	0.336 8	0.420 0	0.830 1	1.232 2	1.627 8	2.017 5
80	0.004 1	0.020 3	0.040 6	0.081 1	0.161 6	0.241 8	0.321 4	0.400 7	0.791 2	1.173 8	1.549 5	1.919 6
90	0.003 8	0.018 8	0.037 6	0.075 0	0.149 4	0.223 3	0.296 6	0.369 6	0.728 1	1.078 0	1.421 1	1.758 0
100	0.975 7	0.017 7	0.035 4	0.070 5	0.140 4	0.209 6	0.278 3	0.346 4	0.679 8	1.004 0	1.320 6	1.630 9
120	0.985 5	0.924 6	0.836 7	0.066 0	0.130 2	0.193 5	0.255 8	0.317 3	0.614 8	0.899 9	1.176 2	1.445 6
140	0.991 1	0.953 5	0.903 4	0.785 2	0.133 4	0.194 0	0.252 7	0.309 9	0.581 5	0.837 4	1.083 2	1.321 4
160	0.993 9	0.969 7	0.937 9	0.868 9	0.699 1	0.372 5	0.296 9	0.337 8	0.576 6	0.805 8	1.024 9	1.236 4
180	0.996 0	0.979 3	0.957 9	0.913 4	0.816 7	0.769 6	0.595 4	0.510 6	0.604 3	0.802 5	0.999 0	1.188 8
200	0.997 0	0.985 3	0.970 5	0.939 9	0.876 8	0.814 0	0.753 4	0.699 7	0.672 0	0.820 4	0.990 7	1.162 3
250	0.998 7	0.993 8	0.987 0	0.973 6	0.947 7	0.923 7	0.903 0	0.885 8	0.856 3	0.917 2	1.022 2	1.143 1
300	0.999 4	0.996 8	0.994 1	0.988 4	0.977 1	0.967 6	0.959 7	0.954 2	0.956 0	0.997 2	1.068 9	1.157 2
350	0.999 8	0.999 0	0.997 9	0.996 1	0.991 9	0.989 0	0.987 0	0.987 0	1.004 9	1.045 1	1.102 3	1.172 2
400	1.000 0	1.000 0	1.000 0	1.000 0	1.000 3	1.001 1	1.002 4	1.004 5	1.030 5	1.071 8	1.122 7	1.181 6
450	1.000 2	1.000 7	1.001 5	1.002 4	1.004 8	1.007 4	1.010 6	1.015 2	1.044 5	1.085 9	1.133 4	1.185 9
500	1.000 2	1.001 1	1.002 2	1.003 8	1.007 5	1.011 5	1.016 1	1.020 7	1.052 3	1.092 7	1.138 0	1.186 6
600	1.000 3	1.001 4	1.002 4	1.005 2	1.010.2	1.015 3	1.020 7	1.026 6	1.058 2	1.096 1	1.137 4	1.180 3
800	1.000 3	1.001 4	1.002 6	1.005 5	1.010 9	1.016 4	1.021 9	1.027 1	1.056 5	1.088 8	1.123 1	1.158 2
1 000	1.000 3	1.001 3	1.002 6	1.005 3	1.010 1	1.014 9	1.019 8	1.025 3	1.050 7	1.078 3	1.107 2	1.136 9

OXYGEN DIFLUORIDE

(Synonyms: Difluorine Monoxide; Fluorine Monoxide)
(Formula: OF_2)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.053 996 2 kg
One Mole of OF_2	0.053 996 2 kg
Specific Volume @ 21.1 °C, 101.325 kPa	447.0 dm^3/kg; 7.16 ft^3/lb
Boiling Point @ 101.325 kPa	128.25 °K; −144.9 °C; −228.8 °F
Freezing Point in Air @ 101.325 kPa	49.35 °K; −223.8 °C; −370.8 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	2.22 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.88
Density, Liquid @ −144.9 °C	1.521 kg/l
Critical Temperature	215.15 °K; −58.0 °C; −72.4 °F
Critical Pressure	4 955 kPa; 49.55 bar; 718.6 psia; 48.9 atm
Critical Volume	1.808 dm^3/kg
Critical Density	0.553 kg/dm^3
Critical Compressibility Factor	0.270
Dipole Moment, Gas	991×10^{-33} C.m; 0.297 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	43.286 J/(mol·°K)
Solubility In Water @ 101.325 kPa @ 0 °C	6.8 cm^3/100 cm^3 water
Trouton Constant	20.6

Description

At room and atmospheric pressure, oxygen difluoride is a colorless toxic gas with a foul odor. It has strong oxidizing characteristics, similar to fluorine. It is shipped in steel cylinders as a nonliquefied gas.

Specifications

Commercially availabe oxygen difluoride has a minimum purity of 98.5%.

Uses

Oxygen difluoride is of interest as an oxidizing agent, especially as an ingredient of high energy rocket-propellant systems.

Toxicity

Oxygen difluoride is a highly toxic gas, somewhat more toxic than fluorine. The 1979 American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a Threshold Limit Value of 0.05 ppm (0.1 mg/m^3). Oxygen difluoride is a pulmonary irritant and can cause pulmonary edema. Difficulty in breathing may not begin until several hours after inhalation and may persist for hours. While the odor of oxygen difluoride is detectable in low concentrations (0.1–0.5 ppm); this is above the Threshold Limit Value and thus odor cannot be relied upon as an adequate warning property.

Precautions in Handling and Storage

Oxygen difluoride is a powerful oxidizer and should not be stored with reducing agents, or other highly oxidizable or flammable materials.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Equipment to contain oxygen difluoride should preferably be pretested with a dry, inert gas such as nitrogen. Leaks which may develop subsequently may be detected by applying soap water solution to the suspected sites (leaks will be evident by bubble formation) or by holding moist starch-iodide paper near the suspected point.

Analtyical Procedures

Oxygen difluoride can be determined by infrared, nuclear magnetic resonance, or mass spectroscopy. Purity may be determined by vapor pressure measurements. It may also be determined by reaction with acidified potassium iodide solution, followed by titration of the liberated iodine.

Materials of Construction

Oxygen difluoride may be handled in glass, stainless steel, copper, monel, or nickel at temperatures up to 200 °C. Only nickel and monel are recommended for higher temperatures.

Matheson

However, the process equipment must be scrupulously cleaned to remove such contaminants as dirt, moisture, oil, grease, slag, and pipe dope and should be passivated with fluorine before contact with oxygen difluoride.

Cylinder and Valve Description

Oxygen difluoride is shipped in DOT approved steel cylinders. The cylinders have brass valves with the approved standard Compressed Gas Association (CGA) valve outlet connection No. 679. The valve outlet has a thread size of 1.030", with left-hand external threads. The mating connection seats on a flat washer (see Figure 1 for details).

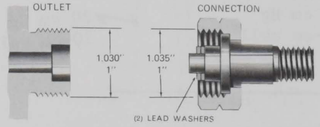


Fig. 1. CONNECTION 679 1.030"-14 LH EXT. using Small Flat Seat with Washer

Recommended Controls

Automatic Pressure Regulators

Matheson has the following corrosion resistant, single stage regulator available for use with oxygen difluoride.

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
B15F-679	28–345	0.28–3.45	4–50

This regulator has a chemically-deposited pure nickel on brass body, a chemically-deposited pure nickel on nickel-silver alloy diaphragm, an aluminum seat, and internal parts of monel. This regulator is supplied with a unique arrangement of aluminum-silicon-bronze valves to allow purging the system with nitrogen prior to or after use.

Manual Controls

Matheson needle valve Model 55F-679 is available for direct attachment to the cylinder valve outlet. This needle valve is of monel stock, and is equipped with a ¼" tube fitting on the outlet.

It should be used only where manual flow control is needed. It should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed.

Flowmeters

Matheson monel Mass Flowmeter Model 8116 is recommended as is the Matheson Fluorine Flowmeter Model 7825. With Model 7825, however, it should be noted that a gradual inevitable etching of the Pyrex flowmeter tube may take place.

For mass flow control, the Matheson Model 8260 monel mass flow Controller is recommended.

Shipping Regulations

Oxygen difluoride is classified by the DOT as "Compressed Gases, n.o.s." and takes a DOT "Flammable Gas" label.

Commercial Preparation

Oxygen difluoride is prepared by passing fluorine into a dilute aqueous solution of sodium hydroxide. It has also been prepared by electrolysis of 80% aqueous hydrofluoric acid.

Chemical Properties (2)

Many common bulk metals react only to a limited extent when warmed with oxygen difluoride, because of the formation of a passive metal fluoride coating which prevents further attack, while finely divided metals may react completely under the same conditions. Mixtures of oxygen difluoride with carbon, carbon monoxide, methane, hydrogen, or water vapor explode when heated or ignited with an electric spark. The nonmetallic elements bismuth, silicon, phosphorus, sulfur, selenium, tellurium, arsenic, and antimony react vigorously with oxygen difluoride on slight warming to produce fluorides and oxyfluorides. Solid chlorides form the corresponding fluorides. Oxygen difluoride oxidizes aqueous solutions of hydrogen chloride, hydrogen bromide, and hydrogen iodide (and their salts) to give the free halogens. Oxygen difluoride reacts slowly with water or dilute aqueous base at room temperature, but much faster at higher temperatures. Nitric oxide and oxygen difluoride inflame on contact. Sulfur dioxide is oxidized to sulfur trioxide by oxygen difluoride. Chlorine and bromine react with oxygen difluoride, when ignited, to form mixtures of oxygen and halogen fluorides; iodine reacts slowly with oxygen difluoride at room temperature, forming iodine pentafluoride and a complex mixture of iodine oxyfluorides. Tetrafluoroethylene and oxygen difluoride react spontaneously to form hexafluoroethane and carbonyl fluoride. Ethylene and oxygen difluoride may react explosively, but under controlled conditions fluoroethane and 1,2-difluoroethane can be recovered. Organic amines are extensively degraded by oxygen difluoride at room temperature, but primary aliphatic amines in a fluorocarbon solvent at −42 °C are smoothly oxidized to the corresponding nitroso compounds.

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

Oxygen difluoride is a bent molecule, having C_{2v} point group symmetry and a symmetry number of two. The F—O bond distance is 1.412 Å (1.412×10^{-10} m), and the F—O—F bond angle is 103.17°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous oxygen difluoride.

Vapor Pressure (4)

The vapor pressure of the liquid oxygen difluoride from 90.35 °K to 137.55 °K is represented by the following Antoine vapor pressure equation:

Matheson

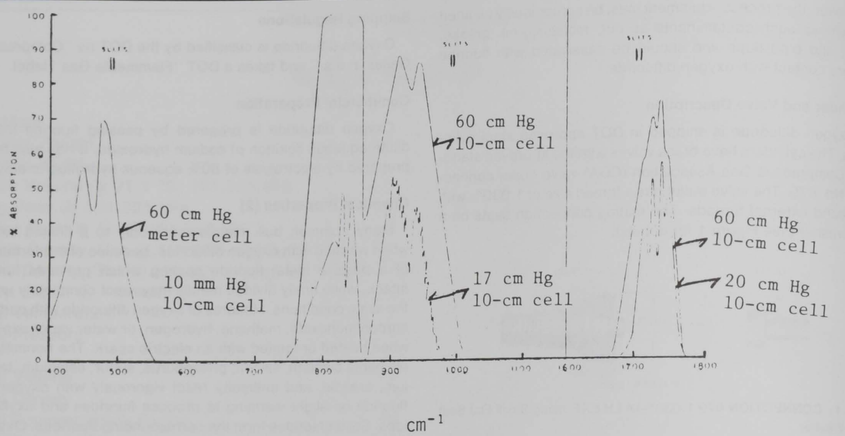


Fig. 2. Infrared spectrum of gaseous oxygen difluoride from 2.5 to 25 μm; cell lengths and pressures are shown in Figure 2; KBr optics (5).

$$\log_{10}p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10}p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.970 1, 491.73, and 265.2, respectively.

Some calculated vapor pressure values are shown below.

Temperature, °K	Vapor Pressure		
	kPa	mbar	mmHg
90.35	1.333	13.3	10
94.75	2.666	26.7	20
99.55	5.333	53.3	40
102.65	7.999	80.0	60
105.05	10.666	107	80
106.95	13.332	133	100
113.25	26.664	267	200
117.45	39.997	400	300
120.55	53.329	533	400
123.05	66.661	667	500
125.25	79.993	800	600
127.15	93.325	933	700
128.25	101.325	1 013.25	760
128.85	106.658	1 067	800
130.45	119.990	1 200	900
131.85	133.322	1 333	1 000
134.35	159.986	1 600	1 200
137.55	199.983	2 000	1 500

Latent Heat of Vaporization @ 128.25 °K 1 108.8 kJ/mol; 265 kcal/mol

Thermodynamic Properties of Oxygen Difluoride As Ideal Gas @ 25 °C (3)

Heat Capacity, C_p°	43.300 J/(mol·°K)
Entropy, S°	247.350 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−247.350 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	10.895 kJ/mol
Enthalpy of Formation, ΔH_f°	24.518 kJ/mol
Free Energy of Formation, ΔF_f°	41.773 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamics and physical properties of oxygen difluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. B. Fox, and R. B. Jackson, in Kirk-Othmer's *Encyclopedia of Chemical Technology, 1966*, Volume 9, pp. 631–632, John Wiley & Sons, Inc., New York, New York.

[3] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[4] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds, 1968* Volume 1, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[5] H. J. Bernstein and J. Powling, *J. Chem. Phys.* 18, 685–689 (1950).

OZONE

(Formula: O_3)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.047 998 2 kg
One Mole of O_3	0.047 998 2 kg
Boiling Point @ 101.325 kPa	161.85 °K; −111.3 °C; −168.3 °F
Freezing Point in Air @ 101.325 kPa	80.65 °K; − 192.5 °C; −314.5 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	1.964 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	1.66
Density, Liquid @ −183 °C	1.574 kg/l
Critical Temperature	261.05 °K; −12.1 °C; 10.2 °F
Critical Pressure	5 532 kPa; 55.32 bar; 802.4 psia; 54.6 atm
Critical Volume	2.292 dm^3/kg
Critical Density	0.436 kg/dm^3
Critical Compressibility Factor	0.280
Dipole Moment, Gas	1.835×10^{-30} C·m; 0.55 D
Viscosity, Liquid @ −183.0 °C	1.57 mPa·s; 1.57 cP
Thermal Conductivity, Liquid @ −183.0 °C	0.222 2 W/(m·°K) 531.1 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −183.0 °C	38.4 mN/m; 38.4 dyn/cm
Solubility In Water @ 101.325 kPa @ 0 °C	49.4 cm^3/100 cm^3 water
Molar Specific Heat, Liquid @ −183.0 °C	85.393 J/(mol·°K)
Dielectric Constant, Liquid @ 90.2 °K	4.79

Description

Pure ozone is a toxic, bluish, unstable, potentially explosive gas or (under refrigeration) dark blue liquid or solid. It has been supplied dissolved in chlorotrifluoromethane ("Freon 13®") in stainless steel cylinders. These solutions can be handled safely at vapor phase concentrations up to 20% by volume of ozone. The cylinder pressure is 3 275 kPa (475 psig) at 20 °C.

Specifications

Ozone is supplied dissolved in a "Freon 13®" solvent with an initial concentration of 50 dm^3 of gaseous ozone (at S.T.P.) per liter of solution. The solutions contain trace amounts of oxygen, which accumulate slowly with ozone decomposition.

Uses

Ozone finds use as an oxidizing agent in organic and inorganic reactions. It is used as a water purification agent, for bleaching Teflon, synthetic fibers, waxes, paper, flour, textiles, oils, etc., for treatment of industrial wastes, for sterilization of air, for deodorization of sewage and stack gases, and for preservation of food in cold storage. Ozone has high germicidal activity on many bacterial organisms. Algae and certain fungus growths not destroyed by chlorine are highly susceptible to ozone treatment.

Effects in Man and Toxicity (2)

Symptoms of acute ozone toxicity appear at a concentration of about 1 ppm by volume. The type and severity of symptoms depend on the concentration and duration of exposure. In mild cases or in the early phases of severe cases, symptoms will include one or more of the following: irritation or burning of the eyes, nose, or throat; lassitude; frontal headache; sensation of substernal pressure, constriction or oppression; acid in mouth; and anorexia.

In more severe cases, there may be present dyspnea, cough, choking sensation, tachycardia, vertigo, lowering of blood pressure, severe cramping chest pain, and generalized body pain. Pulmonary edema may develop; the onset of the edema is usually delayed for one or more hours after exposure.

Following severe acute ozone toxicity, recovery is slow. In the few severe human cases reported, 10–14 days of hospitalization were required. In these cases, minimal residual symptoms were present for as long as 9 months, but all cases eventually recovered completely.

The safe level for short human exposure to concentrations of ozone in excess of 0.1 ppm (the threshold limit value) is not known with certainty. Probably 2 ppm is safe for several minutes, provided that no respiratory infection is present. The atmospheric concentration immediately hazardous to life is likewise not known, but inhalation of 50 ppm for 30 minutes would probably be fatal.

The odor threshold of ozone for the normal person is 0.01–0.015 ppm by volume in air.

The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 0.1 ppm (0.2 mg/m^3) for ozone.

First Aid Treatment (2)

Remove the victim to an uncontaminated atmosphere. Control restlessness and pain by the administration of sedatives and anodynes orally. Severe cases may require subcutaneous injections of small doses of meperidine hydrochloride (Demerol) for relief of pain. Give oxygen inhalation by face mask and rebreathing bag if dyspnea (labored breathing) is acute or accompanied by cyanosis. Keep victim under observation with symptomatic care until the acute symptoms have subsided. Severe cases require hospitalization since deferred pulmonary edema may develop.

Precautions in Handling and Storage

Ozone is supplied dissolved in "Freon-13®" which decreases the hazards of handling and using the gas. Since ozone is a gas which has a tendency to decompose, it is essential that the container be stored at low temperatures to decrease the amount of decomposition. To effect this low temperature storage during delivery the cylinder is packed with *dry ice* in an insulated container which is capable of maintaining low temperatures for approximately 5 days (see Fig. 1).

Upon receipt of the ozone package it is recommended that a fresh charge of *dry ice* be put around the cylinder and the unit recharged periodically until the ozone has been expended or the experiment completed. The ozone cylinder can also be stored in a laboratory deep freeze or *dry ice* chest.

(NOTE: Permitting the ozone to warm up unnecessarily is not a hazard, but will only result in a more rapid decomposition of the ozone, with the half-life being about 3 days. See Table I.)

Table I

Temperature	Approximate Half-Life of Ozone
20 °C	3 days
−15 °C	8 days
−25 °C	18 days
−50 °C	3 months

Using Ozone

Ozone can be removed from the cylinder either in the vapor phase or in the liquid phase. Although ozone is more readily withdrawn as a vapor several disadvantages are apparent. Initially the concentration of ozone which should be about 15 mole % will be diluted by the presence of oxygen from decomposed ozone. There will be a gradual diminishing of ozone concentration as the ozone is withdrawn. To utilize gaseous ozone it is suggested that the cylinder be removed from the dry ice storage and the control regulator or valve attached to the cylinder valve outlet. The gaseous product may be withdrawn as needed with the cylinder in the normal upright position (see Fig. 2). To maintain the ozone concentration remaining in the cylinder it is necessary to return the cylinder to refrigerated storage.

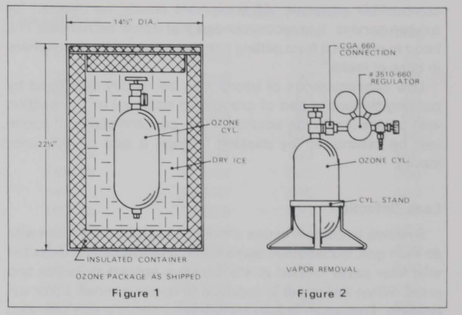


Figure 1

Figure 2

If it is necessary to maintain a relatively constant ozone vapor phase concentration (about 8 mole %) throughout the run, the cylinder should be inverted so that the valve outlet is on the bottom and a vaporizing coil and regulator attached to the valve outlet (see Fig. 3). The cylinder valve may now be opened and the regulator adjusted to discharge ozone into the system as required. When the run is completed return the cylinder to refrigerated storage.

Ozone may also be used dissolved in the liquid "Freon-13®" carrier, by simply withdrawing the chilled material from an inverted cylinder into a chilled receiver (see Fig. 4). Use a needle valve for controlled withdrawal. Return the cylinder to refrigerated storage when the run is completed.

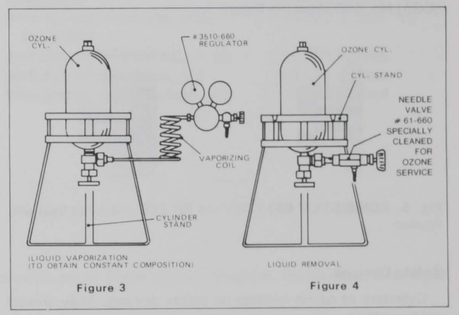


Figure 3

Figure 4

Equipment should be passivated with ozone before use to improve the stability characteristics of the ozone.

Warning

Ozone is a very strong oxidant and particular precautions should be taken to prevent contact with grease, oil or other

combustible materials. All equipment should be cleaned for oxygen service. It is recommended that ozone be handled in a hood to prevent it from getting into the surrounding atmosphere in case of leaks.

Low concentrations of ozone may be readily destroyed by passing through a bed of granulated charcoal or by reaction with potassium iodide solution. High concentrations of ozone can be neutralized by passing through a bed of molecular sieves.

Leak Detection

Systems to contain ozone should be pretested for leaks with an inert gas. Subsequent leaks which develop can be detected with filter paper dipped in 4% aqueous potassium iodide and dried. When this paper is exposed to ozone a brown color will develop. Potassium iodide-impregnated litmus paper can also be used. The paper will turn blue on exposure to ozone.

Materials of Construction

The preferred materials of construction are: glass, stainless steel, Teflon, Kel-F, viton or hypalon, aluminum, tygon, polyvinyl chloride and polyethylene. The use of copper and copper alloys should be avoided because these materials act as a catalyst to promote decomposition. Rubber or any composition thereof is unsuitable. Extreme precaution should be taken to avoid contact with oil, grease or other readily combustible substances.

Cylinder and Valve Description

Ozone is supplied in stainless steel cylinders equipped with a valve outlet designated as Compressed Gas Association (CGA) No. 660 shown in Figure 5.

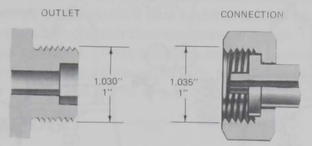


Fig. 5. CONNECTION 660 1.030″-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders of ozone contain no safety devices. They should not be stored near radiators or other sources of heat.

Recommended Controls

Automatic Pressure Regulator

An automatic, stainless steel, pressure regulator with a stainless steel diaphragm is recommended for use when handling gaseous mixtures of ozone. Matheson Model 3500-660 regulator is recommended for this service.

Manual Controls

Matheson valve Model 61A-660 is recommended for manual control of either gaseous or liquid ozone. This control must be specially cleaned for ozone service.

Shipping Regulations

Ozone is shipped in stainless steel cylinders as a non-flammable compressed gas, taking a DOT "Green Label."

Chemical Preparation

Ozone can be prepared by passing oxygen through an electric discharge or exposing it to ultraviolet radiation. Ozone is also produced in certain reactions where molecular oxygen is formed, e.g., the action of fluorine on water or the electrolysis of concentrated H_2SO_4 at high current densities.

Chemical Properties

Ozone is second only to fluorine in its oxidizing power. It oxidizes most inorganic compounds to their final oxidative state. For example, ferrous, manganous, and chromous ions are oxidized quantitatively to their respective highest states of oxidation. The addition of ozone to an ethylenic double bond followed by decomposition of the resulting ozonide has long been recognized as the most reliable laboratory procedure for oxidative cleavage, permitting location of the double bond. As a method of cleavage, the above ozonolysis has the important advantage in that it permits isolation of the primary cleavage products, since the oxidant (ozone) can be removed before the ozonide is cleaved.

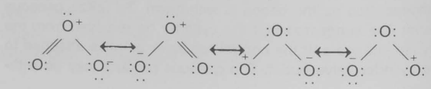
Ozonolysis has been extensively used in the laboratory for structural analysis and has also found commercial application for the production of aldehydes and acids. The application of this method has been limited to some extent by the fact that many ozonides are explosive. Explosions can usually be avoided by working at low temperatures (in solvents such as chlorofluoromethane or ethanes, ethyl acetate, carbon tetrachloride, or ethyl chloride) and by carrying out the ozonide formation and decomposition in solution, without attempting to isolate the ozonide itself.

In the past few years, commercial processes for the synthesis of cortisone and other hormones have utilized ozonolysis to effect degradation of an olefinic side chain. Ozone is also being used commercially for the oxidation of oleic acid to azelaic and perlargonic acids.

Thermodynamic and Detailed Physical Data

Molecular Structure

Ozone is a bent molecule, with C_{2v} point group symmetry and a symmetry number of two (3). The O—O bond distance is 1.278 Å (1.278×10^{-10} m) and the O—O—O bond angle is 116.8° (4). These parameters suggest a structure which involves resonance among the following forms (4):



Infrared Spectrum

See Figure 6 for the far infrared spectrum of gaseous ozone.

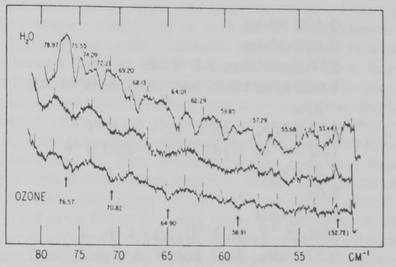


Fig. 6. Far infrared spectrum of gaseous ozone; 9-cm cell with 1-mm crystal quartz windows; starting cell pressure 67.55 kPa (506.7 mmHg). The center curve gives the background for the ozone run directly below. The upper curve, illustrating strong water absorption, is included for comparison (6).

Vapor Pressure (5)

The vapor pressure of liquid ozone between 117.15 °K and 173.15 °K is represented by the following Antoine vapor equation:

$$\log_{10} p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.837, 552.5, and 251.0, respectively.

Some calculated vapor pressure values are shown below.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
117.15	1.333	13.3	10
122.15	2.666	26.7	20
128.15	5.333	53.3	40
131.15	7.999	80.0	60
134.15	10.666	107	80
136.15	13.332	133	100
144.15	26.664	267	200
149.15	39.997	400	300
152.65	53.329	533	400
155.65	66.661	667	500
158.25	79.993	800	600
160.55	93.325	933	700
161.85	101.325	1 013.25	760
162.55	106.658	1 067	800
164.45	119.990	1 200	900
166.15	133.322	1 333	1 000
169.15	159.986	1 600	1 200
173.15	199.983	2 000	1 500

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/mol
90.15	15.272
161.85	14.196

Thermodynamic Properties of Ozone As Ideal Gas @ 25 °C (3)

Heat Capacity, C_p^o	39.238 J/(mol·°K)
Entropy, S^o	238.823 J/(mol·°K)
Free Energy Function, $(F^o_{298} - H^o_{298})/298$	−238.823 J/(mol·°K)
Enthalpy Difference, $H^o_{298} - H^o_0$	10.351 kJ/mol
Enthalpy of Formation, ΔH_f^o	142.674 kJ/mol
Free Energy of Formation, ΔF_f^o	163.163 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of ozone, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 128–132, Matheson, Lyndhurst, New Jersey.

[3] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[4] J. J. Lagowski, *Modern Inorganic Chemistry*, *1973*, pp. 460–462, Marcel Dekker, Inc., New York, New York.

[5] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds*, *1968*, Volume 1, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[6] A. Danti and R. C. Lord, *J. Chem. Phys.* 30, 1310–1313 (1959).

PERCHLORYL FLUORIDE

(Formula: ClO_3F)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.102 45 kg
One Mole of ClO_3F	0.102 45 kg
Specific Volume @ 21.1 °C, 101.325 kPa	237.2 dm^3/kg; 3.8 ft^3/lb
Vapor Pressure @ 20 °C	1 062 kPa; 10.62 bar; 154.1 psia; 10.49 atm
Boiling Point @ 101.325 kPa	226.48 °K; −46.7 °C; −52.0 °F
Melting Point	125.45 °K; −147.7 °C; −233.9 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	4.315 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	3.64
Density, Liquid @ Saturation Pressure @ 25 °C	1.412 kg/l
Critical Temperature	368.35 °K; 95.2 °C; 203.4 °F
Critical Pressure	5 370 kPa; 53.7 bar; 778.9 psia; 53.0 atm
Critical Volume	1.570 dm^3/kg
Critical Density	0.637 kg/dm^3
Critical Compressibility Factor	0.282
Latent Heat of Fusion @ −147.7 °C	3.834 kJ/mol; 916.3 cal/mol
Dipole Moment, Gas	76.7×10^{-33} C·m; 0.023 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	64.898 J/(mol·°K)
@ Constant Volume	57.944 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.12
Molar Specific Heat, Liquid @ −147.7 °C	87.873 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.014 89 mPa·s; 0.014 89 cP
Viscosity, Liquid @ −46.7 °C	0.145 mPa·s; 0.145 cP
Surface Tension @ −46.7 °C	20.7 mN/m; 20.7 dyn/cm
Solubility In Water @ 101.325 kPa @ 25 °C	0.000 6 kg/l of solution

Description

At room temperature and atmospheric pressure, perchloryl fluoride is a colorless, nonflammable, toxic gas, with a characteristic sweet odor. It is a compound of high thermal stability, low reactivity (at room temperature), and high oxidizing potential. It is shipped in cylinders as a liquefied gas under its own vapor pressure of 960 kPa (139 psig) at 20 °C.

Specifications

Perchloryl fluoride has a minimum purity of 98.5 mole %.

Uses

The major use of perchloryl fluoride is in blends with halogen fluorides as a liquid oxidizer for rocket engines. It is also used for the selective fluorination of steroids.

Effects In Man and Toxicity (2)

Perchloryl fluoride is a toxic gas. The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 3 ppm (14 mg/m^3) for perchloryl fluoride (concentration in air to which nearly all workers may be exposed, day after day, without adverse affects). Moderate to high concentrations of the vapor cause respiratory irritation and methemoglobinemia and possibly cyanosis. It is absorbed through the skin, and liquid contact may cause frostbite. Repeated long-term exposure to low concentrations of perchloryl fluoride may cause fluorosis or fluoride deposition in bones and teeth. Its odor can be detected in concentrations as low as 10 ppm but this cannot be relied upon as an indication of toxic concentrations in the air.

First Aid Suggestions

The procedures outlined for exposure to fluorine should be followed.

Precautions in Handling and Storage

Preparations involving perchloryl fluoride should be conducted in a well-ventilated hood behind adequate safety shields. Equipment design should be such that control of the reaction can be maintained without removing safety shields. Mixtures with oxidizable substances, if ignited by spark, flame, sufficient heat, or sometimes by impact, can cause serious explosions. Handling precautions for perchloryl fluoride are similar to those for liquid and gaseous oxygen. Liquid perchloryl fluoride must never be permitted to accumulate in the presence of any readily oxidizable materials such as organic compounds. Neither liquid nor gaseous perchloryl fluoride should be permitted to come into contact with oxidizable materials of high specific surface area such as carbon, charcoal, sawdust, cloth, paper, etc., since spontaneous ignition may occur even at low temperatures. If access is necessary to areas contaminated by high concentrations of perchloryl fluoride vapor, only self-contained breathing apparatus must be used. Gas masks which might contain activated carbon should not be used since the carbon may ignite spontaneously in atmospheres containing high concentrations of perchloryl fluoride vapor. Before isolating and handling perchloryl derivatives, both organic and inorganic, extreme caution should be exercised until the shock and heat sensitivity of the compound has been thoroughly characterized.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Lines and equipment to contain perchloryl fluoride should be pretested for leaks with a dry inert gas such as nitrogen. Leaks can be detected by painting the suspected sites with soapy water; leaks will be indicated by bubble formation.

Analytical Detection

Perchloryl fluoride in the atmosphere may be determined quantitatively by absorbing a known volume of the atmosphere in a 2% solution of potassium hydroxide in 98% ethanol. It is rapidly and completely hydrolyzed, precipitating potassium perchlorate.

Disposal of Leaking Cylinders

Should it become necessary to dispose of leaking cylinders containing perchloryl fluoride, the following procedure may be used. Put on self-contained breathing equipment. Remove cylinder to a well-ventilated hood. Attach appropriate regulator and check valve. Introduce the gas at a moderate rate into an adequate amount of a 20% solution of potassium hydroxide in 90% ethanol.

Materials of Construction

Dry perchloryl fluoride does not attack glass or the majority of metals at ordinary temperatures. Many gasketing materials are embrittled by long contact with the gas; however, Teflon and Kel-F are unaffected. At high temperatures, most organic materials and some metals can be ignited in perchloryl fluoride. Under very severe shock, some metals, e.g., titanium, show deflagration in contact with perchloryl fluoride.

Cylinder and Valve Description

Cylinders of perchloryl fluoride are equipped with brass valves with Compressed Gas Association (CGA) outlet connection No. 670. The valve outlet is 1.030″ in diameter with left-hand external threads (see Figure 1 for an illustration). Lecture bottles have a special 5/16″-32 threads per inch, female outlet.

CONNECTION 670 1.030″-14 LH EXT. using Flat Seat with Washer

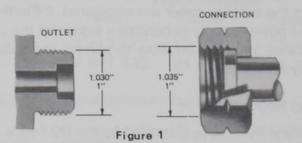


Figure 1

Recommended Controls

Automatic Pressure Regulators

Matheson has the following corrosion resistant, single stage regulators available for use with perchloryl fluoride.

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
B15A-670	28–345	0.28–3.45	4–50
B16A-670	345–4 480	3.45–44.8	50–650

These regulators have chemically-deposited pure nickel on brass bodies, chemically-deposited pure nickel on nickel-silver alloy diaphragms, Kel-F seats, and internal parts and outlet needle valves of monel. Both regulators have ¼″ NPT male outlet connections. A monel check valve (Model 402V) is recommended for use with these regulators to prevent suck-back of foreign materials into the regulator.

Manual Controls

Matheson needle valve Model 55-670 is available for direct attachment to the cylinder valve outlet. These needle valves are of monel bar stock, and may be equipped with a variety of outlets (¼″ tube fitting, ¼″ NPT male or female pipe, or hose connections).

They should be used where manual flow control is needed and should not be used as a pressure control since they will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. A Model 60L monel needle valve is available for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory monel flowmeter units with 150 mm tubes and floats are recommended for use where definite flow rates must be known.

Monel electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8260 of monel is designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas

flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Perchloryl fluoride is classified by the DOT as a nonflammable compressed gas and is shipped under the required "Green Label".

Chemical Preparation

Several methods have been used to prepare perchloryl fluoride.

1. Electrolysis of a solution of sodium perchlorate in anhydrous hydrogen fluoride.
2. Reaction of potassium chlorate with fluorine.
3. Reaction of potassium perchlorate with antimony pentafluoride.
4. Heating a solution of potassium perchlorate in fluorosulfonic acid.

Chemical Properties

Perchloryl fluoride has high thermal stability, measurable decomposition rates being found above about 470 °C. Perchloryl fluoride is very resistant to hydrolysis. Hardly any reaction with water occurs even at 300 °C under pressure, and 10% alkali hydroxide solutions effect only a slow reation. Perchloryl fluoride is hydrolyzed quantitatively by concentrated aqueous alkali hydroxide solutions under pressure at 300 °C. Alcoholic solutions of alkali hydroxides rapidly and completely hydrolyze perchloryl fluoride. Perchloryl fluoride is unreactive at room temperature with a considerable number of chemicals such as nitric oxide, hydrogen sulfide, vinylidene chloride, phosphorus trichloride, sulfur dichloride, and hydrocarbons, but at 100–300 °C these chemicals react explosively with perchloryl fluoride. Perchloryl fluoride reacts with aromatic compounds in the presence of Friedel-Crafts catalysts to give compounds containing the perchloryl radical, —ClO_3. Finally, perchloryl fluoride specifically fluorinates steroids to give fluorine-containing steroids.

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

Perchloryl fluoride has C_{3v} point group symmetry and a symmetry number of three. The bond distances and angles are as follows: F—Cl 1.63 Å (1.63 × 10^{-10} m); O—Cl 1.46 Å (1.46 × 10^{-10} m); F—Cl—O 95.17 °; O—Cl—O 119.2 °.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous perchloryl fluoride.

Vapor Pressure (4)

The vapor pressure of liquid perchloryl fluoride from 163.55 °K to 242.13 °K is represented by the following Antoine vapor pressure equation:

$$\log_{10} p = A - \frac{B}{C + t} \quad \text{or} \quad t = \frac{B}{A - \log_{10} p} - C$$

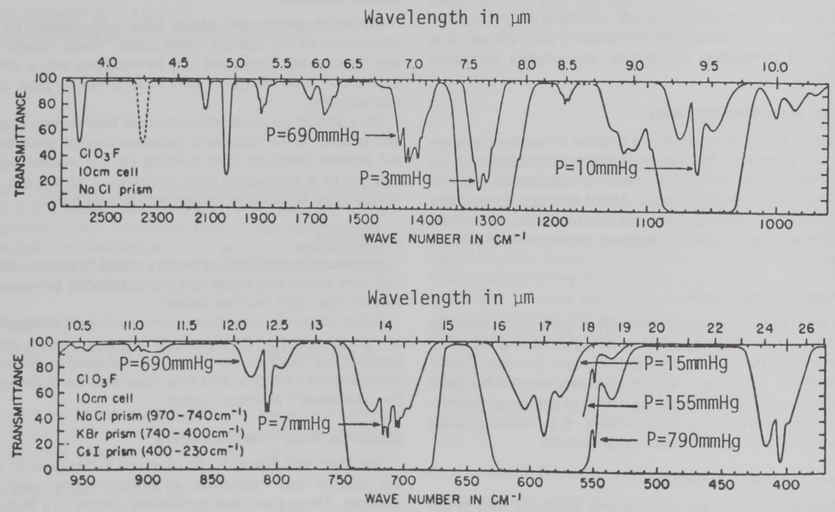


Fig. 2. Infrared spectrum of gaseous perchloryl fluoride; relevant details are indicated in the figure (6).

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.889 58, 789.768, and 243.70, respectively.

Some calulated vapor pressures are shown below, as well as some additional values at higher temperatures.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
163.55	1.333	13.3	10
170.77	2.666	26.7	20
178.81	5.333	53.3	40
183.96	7.999	80.0	60
187.83	10.666	107	80
190.97	13.332	133	100
201.57	26.664	267	200
208.44	39.997	400	300
213.65	53.329	533	400
217.91	66.661	667	500
221.54	79.993	800	600
224.72	93.325	933	700
226.46	101.325	1 013.25	760
227.56	106.658	1 067	800
230.14	119.990	1 200	900
232.50	133.322	1 333	1 000
236.72	159.986	1 600	1 200
242.13	199.983	2 000	1 500
273.15	579.229	5 792	4 345 (5)

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
298.15	1 213.477	12 135	9 102 (5)
327.59	2 447.639	24 476	18 359 (5)

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv

Temperature, °K	Hv, kJ/mol
175.13	21.732
200.15	20.620
226.48	19.326

Thermodynamic Properties of Perchloryl Fluoride As Ideal Gas @ 25 °C (3)

Heat Capacity, C_p°	64.923 J/(mol·°K)
Entropy, S°	278.876 J/(mol·°K)
Free Energy Function ($F_{298}^\circ - H_{298}^\circ$)/298	−278.876 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	13.297 kJ/mol
Enthalpy of Formation, ΔH_f°	−21.422 kJ/mol
Free Energy of Formation, ΔF_f°	50.585 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of perchloryl fluoride, see W. Braker and A. M. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, **Effects of Exposure to Toxic Gases—First Aid and Medical Treatment**, 2nd edition, *1977*, pp. 132–134, Matheson, Lyndhurst, New Jersey.

[3] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U.S. Government Printing Office, Washington, D. C.

[4] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds*, *1968*, Volume 1, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[5] R. L. Jarry and J. J. Fritz, *Chem. Eng. Data Ser.* 3, 34 (1958).

[6] D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.* 25, pp. 1128–1131 (1956).

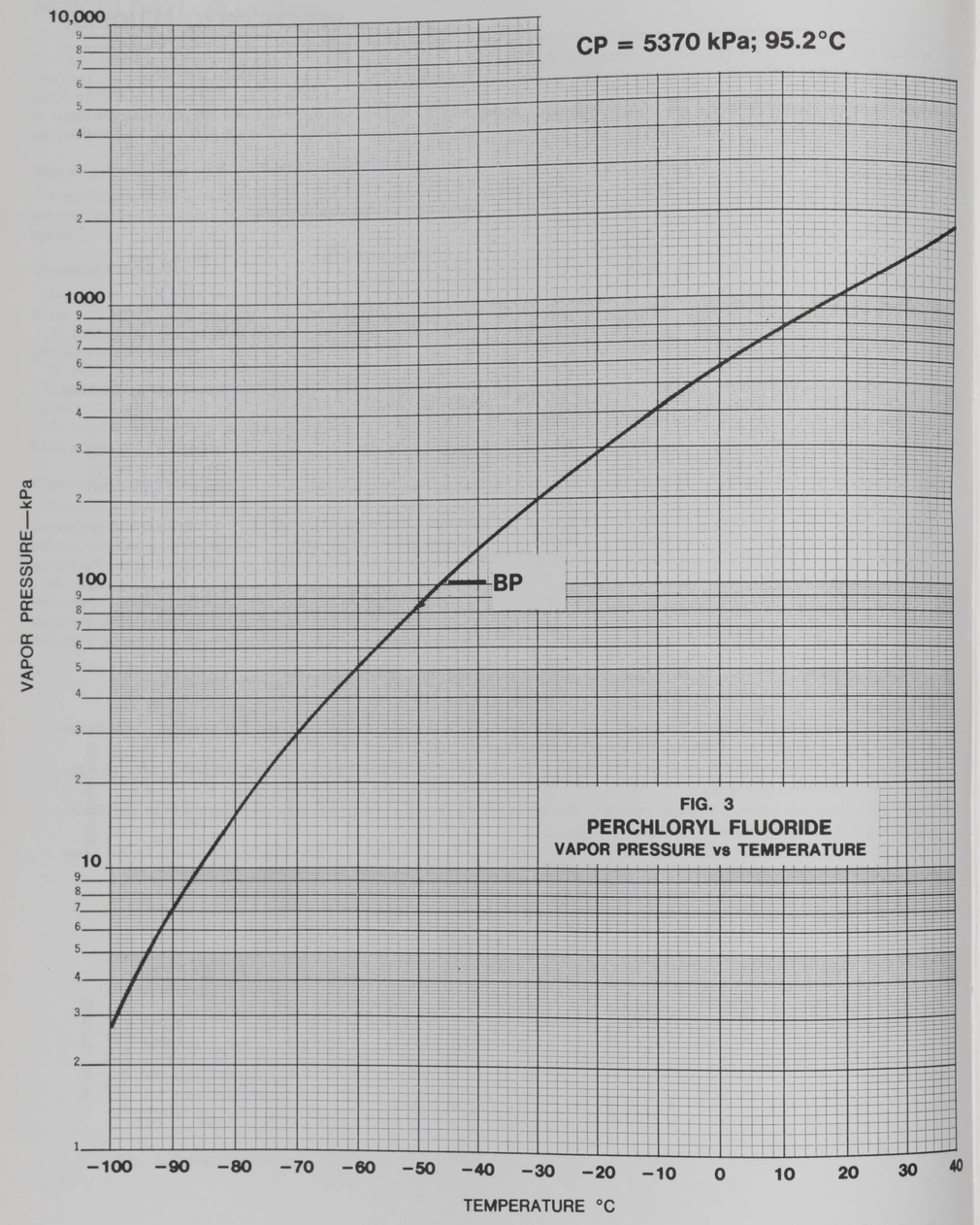


FIG. 3
PERCHLORYL FLUORIDE
VAPOR PRESSURE vs TEMPERATURE

PERFLUOROBUTANE

(Synonyms: Perfluoro-n-butane; Decafluorobutane)
(Formula: C_4F_{10})

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.238 028 kg
One Mole of C_4F_{10}	0.238 028 kg
Specific Volume @ 21.1 °C, 101.325 kPa	101.1 dm^3/kg; 1.62 ft^3/lb
Vapor Pressure @ 31.7 °C	330kPa; 3.3 bar; 47.9 psia; 3.26 atm
Boiling Point @ 101.325 kPa	271.15 °K; −2.0 °C; 28.4 °F
Freezing Point	144.95 °K; −128.2 °C; −198.8 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	9.935 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	8.39
Density, Liquid @ Saturation Pressure @ 20 °C	1.517 kg/l
Critical Temperature	386.35 °K; 113.2 °C; 235.8 °F
Critical Pressure	2 323 kPa; 23.23 bar; 337.0 psia; 22.93 atm
Critical Volume	1.588 dm^3/kg
Critical Density	0.630 kg/dm^3
Critical Compressibility Factor	0.273
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.012 89 mPa·s; 0.012 89 cP

Description

Perfluorobutane is a colorless, nontoxic, nonflammable gas. It is shipped in steel cylinders as a liquefied gas under its own vapor pressure of 230 kPa (33.3 psig) at 31.7 °C.

Specifications

Perfluorobutane is available with a minimum purity of 99.0 mole %.

Uses

Perfluorobutane is primarily of interest as a dielectric gas.

Toxicity

Preliminary toxicological investigation has shown perfluorobutane to be nontoxic.

Precautions in Handling and Storage

The rules listed in Appendix I should be observed.

Leak Detection

Leaks of perfluorobutane in lines and equipment may be detected by painting the suspected sites with soap water solution; leaks will be indicated by bubble formation.

Disposal of Leaking Cylinders

See Appendix II-C for disposal procedure.

Materials of Construction

Since perfluorobutane is a noncorrosive gas, any common or commercially available metal may be used. However, piping systems or vessels to contain perfluorobutane should be designed to withstand the pressures to be encountered.

Cylinder and Valve Description

Perfluorobutane is shipped in DOT approved steel cylinders. Cylinders of perfluorobutane are equipped with valves having Compressed Gas Association (CGA) valve outlet No. 668, which has a thread size of 1.030 inches diameter, right-hand external threads, using a washer as a seal (see Figure 1). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet.

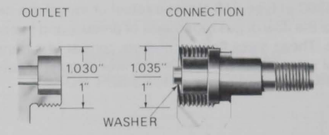


Fig. 1. CONNECTION 668 1.030"-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders of perfluorobutane have safety devices of fusible metal plugs, melting at about 73.9 °C (165 °F).

PERFLUOROBUTANE

Recommended Controls

Automatic Pressure Regulators

Matheson regulator Model 1P-668 is recommended for use with perfluorobutane. This regulator has a brass body, brass internal parts, neoprene diaphragm, and a neoprene seat. It has a delivery pressure range of 28–240 kPa (4–35 psig). For low pressure regulation, Matheson supplies a Model 70 regulator, which is constructed of an aluminum body and a Buna N diaphragm, and with an oversized, pancake body to allow sensitive and accurate low pressure control. Three pressure ranges are available.

Model No.	Delivery Pressure Range kPa	mbar (g)	psig
70B-668	0.5–3.0	5–30	2–12 inches water column
70-668	3.4–34.5	34–345	0.5–5.0 psig
70A-668	34.5–68.9	345–689	5–10 psig

Manual Controls

Manual needle valve Model 50-668 is available for direct attachment to the cylinder valve outlet. This valve can be equipped with a variety of outlets, such as a hose connection, ¼″ tube fitting, or ¼″ NPT male or female pipe. It should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. Matheson needle valves Model 30AR and 31B are recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of presure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Perfluorobutane is classified by the DOT as a nonflammable compressed gas and is shipped with the required "Green Label".

Chemical Preparation

Perfluorobutane is prepared by fluorination of butane with cobalt trifluoride at elevated temperatures.

Chemical Properties

Perfluorobutane is essentially chemically unreactive.

Thermodynamic and Detailed Physical Data

Vapor Pressure (2)

Temperature, °K	Vapor Pressure kPa	bar	atm
233.27	16.617	0.166	0.164
241.24	25.737	0.257	0.254
248.83	37.693	0.377	0.372
257.88	57.654	0.577	0.569
269.24	93.827	0.938	0.926
304.88	330.320	3.30	3.26
312.85	414.419	4.14	4.09
323.56	562.354	5.62	5.55
333.62	732.580	7.33	7.23
343.17	920.031	9.20	9.08
358.32	1 303.040	13.0	12.86
373.41	1 792.439	17.9	17.69
383.04	2 178.488	21.8	21.50

See Figure 2 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv (2)

Temperature, °K	ΔHv, kJ/mol
233.15	25.522
253.15	24.058
271.15	22.928
273.15	22.845

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of perfluorobutane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] J. A. Brown and W. H. Mears, *J. Phys. Chem.* 62, 960 (1958).

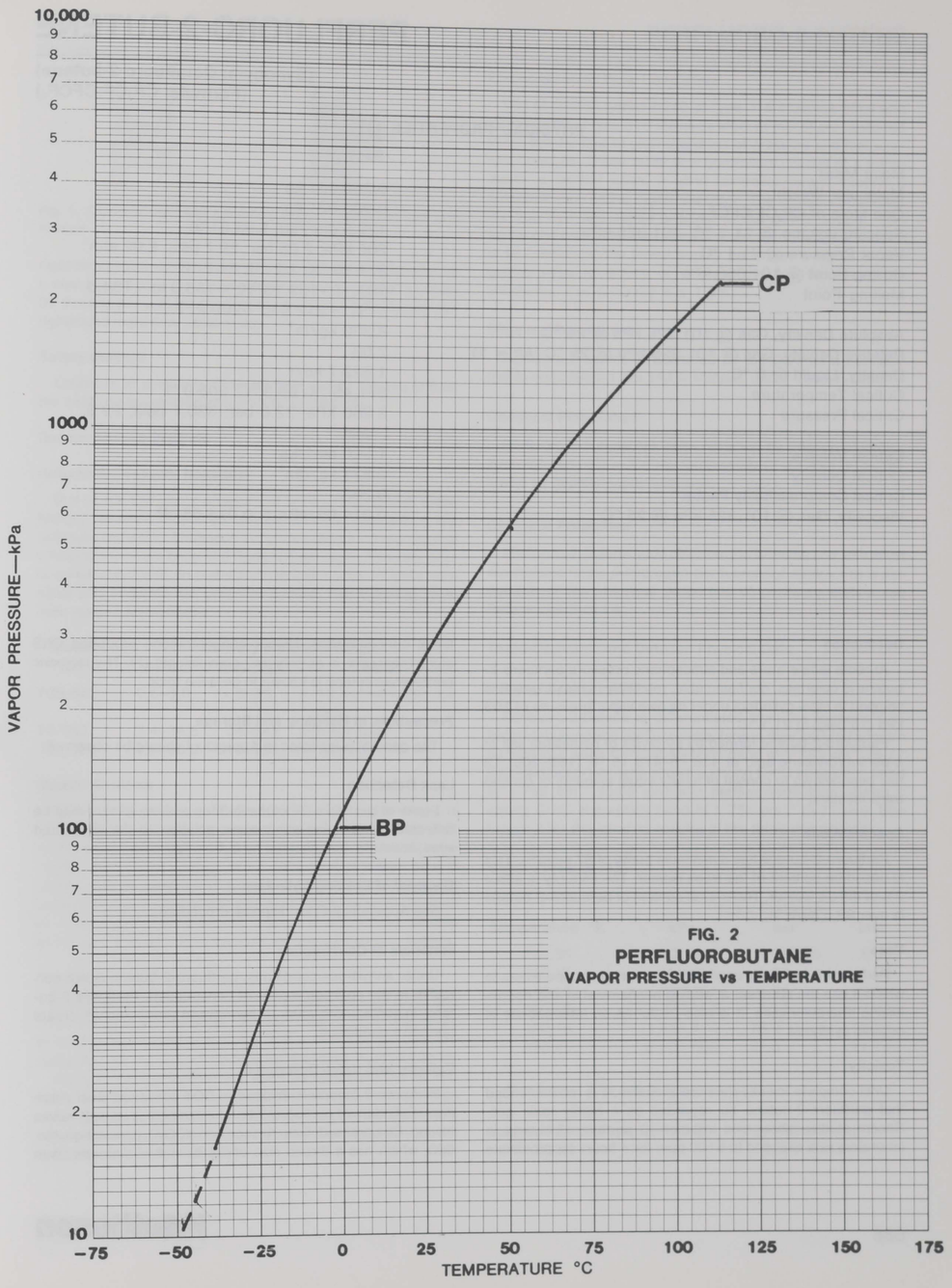


FIG. 2
PERFLUOROBUTANE
VAPOR PRESSURE vs TEMPERATURE

PERFLUORO-2-BUTENE

(Synonym: Octafluoro-2-butene)
(Formula: $CF_3CF:CFCF_3$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.200 031 kg
One Mole of $CF_3CF:CFCF_3$	0.200 031 kg
Specific Volume @ 21.1 °C, 101.325 kPa	120.5 dm^3/kg; 1.93 ft^3/lb
Vapor Pressure @ 21.1 °C	205 kPa; 2.05 bar; 29.7 psia; 2.02 atm
Boiling Point @ 101.858 kPa	274.35 °K; 1.2 °C; 34.2 °F
Melting Point	137.15 -139.15 °K; −136.0 to −134.0 °C; −212.8 to −209.2 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	8.330 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	7.03
Density, Liquid @ 0 °C	1.529 7 kg/l
Critical Temperature	371.45 °K; 98.3 °C; 208.9 °F
Critical Pressure	2 280 kPa; 22.8 bar; 330.7 psia; 22.5 atm
Critical Volume	1.920 dm^3/kg
Critical Density	0.521 kg/dm^3
Critical Compressibility Factor	0.283
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.014 65 mPa·s; 0.014 65 cP

Description

At room temperature and atmospheric pressure perfluoro-2-butene is colorless, nonflammable, relatively nontoxic gas. It is shipped in steel cylinders under its own vapor pressure of 103 kPa (15 psig) at 21.1 °C.

Perfluoro-2-butene formed by pyrolysis of potassium salt of *n*-perfluoro-valeric acid at 438.15–473.15 °K (165–200 °C) has been shown to consist of nearly equal amounts of cis and trans isomers.

Specifications

Perfluoro-2-butene has a minimum purity of 97 mole %. This is based on content of the trans isomer. The impurity is about 2% of the cis isomer. The overall content of perfluoro-2-butene is over 99.5 mole %.

Uses

Perfluoro-2-butene is used in the formation of copolymers to which it has the potential of adding nonflammable and nonoxidizing characteristics. It is also useful as an intermediate in organic synthesis.

Toxicity

Until complete toxicity data are available, it is recommended that perfluoro-2-butene be regarded as a highly toxic gas. Recent studies show mild irritation to perfluoro-2-butene in laboratory rats exposed to 6100 ppm for 4 hours (approximate lethal concentration). Higher concentrations produced CNS signs (decrease in activity and convulsions) (2). The isomeric perfluoroisobutene is known to be quite toxic.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Leak Detection

Leaks of perfluoro-2-butene in lines and equipment may be detected by applying soap water solution to the suspected sites; leaks will be indicated by bubble formation.

Disposal of Leaking Cylinders

See Appendix II-C for disposal procedure.

Materials of Construction

Under anhydrous conditions, perfluoro-2-butene is not corrosive to the common metals of construction. Perfluoro-2-butene, in contact with water, is hydrolyzed slowly and will create corrosive conditions.

Cylinder and Valve Description

Perfluoro-2-butene is shipped in DOT approved steel cylinders. Cylinders of perfluoro-2-butene are equipped with valves having Compressed Gas Association (CGA) connection No. 660, which has a thread size of 1.030 inches diameter, with

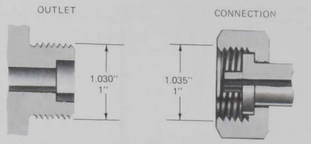


Fig. 1. CONNECTION 660 1.030″-14 RH EXT. using Flat Seat with Washer

right-hand external threads with a flat seat using a washer as a seal (see Figure 1). Lecture bottles have a special 5/16 inch-32 threads per inch female outlet and a 9/16-18 threads per inch right-hand male dual valve outlet.

Safety Devices

Cylinders of perfluoro-2-butene have safety devices of fusible metal plugs, melting about 73.9 °C (165 °F).

Recommended Controls

Automatic Pressure Regulator

Due to the low vapor pressure of perfluoro-2-butene, satisfactory pressure regulation can be obtained only with a low pressure regulator. Matheson supplies a Model 70 regulator of a forged aluminum body and Buna N diaphragm. This regulator is constructed with an oversized, pancake body to allow sensitive and accurate low pressure control. The following pressure ranges are available:

Model No.	Delivery Pressure Range kPa	mbar (g)	psig
70B-660	0.5–3.0	5–30	2–12 inches water column
70-660	3.4–34.5	34–345	0.5–5.0 psig
70A-660	34.5–68.9	345–689	5–10 psig

Manual Controls

Matheson needle valve Model 50-660, of brass bar stock, is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a hose connection, 1/4″ tube fitting, or 1/4″ NPT male or female pipe. It should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. Manual needle valves, Models 30AR and 31B are recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Perfluoro-2-butene is classified by the DOT as a nonflammable compressed gas and is shipped under "Green Label".

Chemical Preparation

Perfluoro-2-butene has been obtained by treating chlorotrifluoroethylene (CF_2:CClF) to form mainly $CF_3CClFCClFCF_3$ followed by dechlorination with zinc.

Chemical Properties

Perfluoro-2-butene adds chlorine and bromine and with alkali alcoholates forms β-hydrogen-perfluoroalkyl ethers. For a discussion of the chemical properties of perfluoro olefins see References 3 and 4.

Thermodynamic and Detailed Physical Data

Infrared Spectrum (5)

Perfluoro-2-butene is differentiated from the isomeric perfluoro-1-butene and perfluoroisobutene in their infrared spectra by having a weak C═C absorption band at 1 733 cm^{-1} (5.77 μm); perfluoro-1-butene shows a strong C═C absorption band at 1 792 cm^{-1} (5.58 μm) and perfluoroisobutene shows a strong C═C absorption band at 1 751 cm^{-1} (5.71 μm). See Figure 2 for the infrared spectra of the three compounds.

Vapor Pressure (1)

Temperature, °K	Vapor Pressure kPa	bar	atm
274.35	101.325	1.013 25	1.00
290.15	192.518	1.93	1.90
310.15	396.181	3.96	3.91
330.15	773.110	7.73	7.63
350.15	1 331.410	13.3	13.14
370.15	2 202.806	22.0	21.74

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization @ 274.35 °K	27.489 kJ/mol; 6.570 kcal/mol

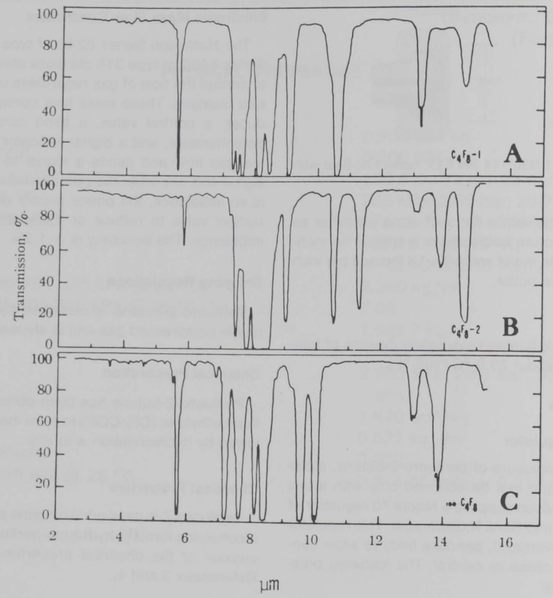


Fig. 2. Infrared spectra of gaseous perfluoro-1-butene (A), perfluoro-2-butene (B), and perfluoroisobutene (C); 2.5-cm cell, with NaCl prism; cell pressure: 6.666 kPa (50 mmHg) (5).

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of perfluoro-2-butene, see W. Braker, and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] Unpublished DuPont data, Haskell Laboratory, 1975.

[3] J. H. Simons, editor, *Fluorine Chemistry, 1950*, pp. 472–8, Academic Press, Inc., New York, New York.

[4] *Advances in Fluorine Chemistry*, M. Stacey, J. C. Tatlow, and A. G. Sharpe, editors, *1965*, Volume 4, Butterworth, Inc., Washington, D. C.

[5] T. J. Brice, *et al.*, *J. Amer. Chem. Soc.* 75, 2698–2702 (1953).

Matheson

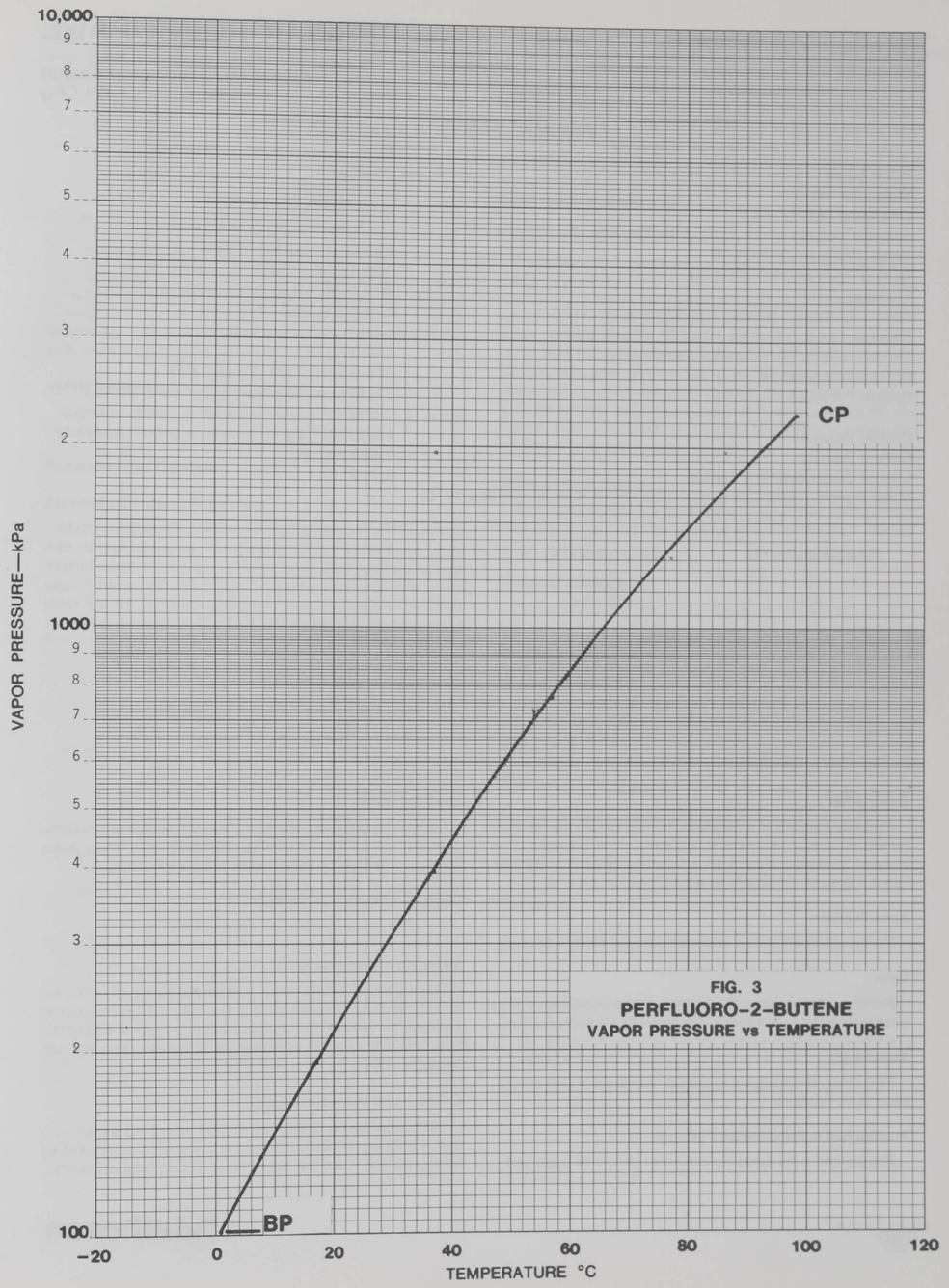


FIG. 3
PERFLUORO-2-BUTENE
VAPOR PRESSURE vs TEMPERATURE

PERFLUOROPROPANE

(Synonym: Octafluoropropane)
(Formula: $CF_3CF_2CF_3$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.188 020 kg
One Mole of $CF_3CF_2CF_3$	0.188 020 kg
Specific Volume @ 21.1 °C, 101.325 kPa	126.1 dm^3/kg; 2.02 ft^3/lb
Vapor Pressure @ 21.1 °C	792 kPa; 7.92 bar; 114.8 psia; 7.8 atm
Boiling Point @ 101.325 kPa	236.45 °K; −36.7 °C; −34.1 °F
Freezing Point	90.15 °K; −183.0 °C; −297.4 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	8.003 5 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C	6.69
Density, Liquid @ Saturation Pressure @ 20 °C	1.352 kg/l
Critical Temperature	345.05 °K; 71.9 °C; 161.4 °F
Critical Pressure	2 680 kPa; 26.8 bar; 388.7 psia; 26.45 atm
Critical Volume	1.590 dm^3/kg
Critical Density	0.629 kg/dm^3
Critical Compressibility Factor	0.279

Molar Specific Heat,Gas @ 101.325 kPa @ Constant Pressure, Cp

Temperature, °C	Cp, J/(mol·°K)
10	145.101
50	156.021

Viscosity, Gas @ 101.325 kPa @ 25 °C	0.014 54 mPa·s; 0.014 54 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.013 81 W/(mol·°K); 33.0×10^{-16} cal·cm/(s·cm^2·°C)

Description

Perfluoropropane is a colorless, nonflammable gas at room temperature and atmospheric pressure. It is nontoxic. It is shipped in steel cylinders as a liquefied gas under its own vapor pressure of 690 kPa (pg) (100 psig) at 21.1 °C.

Specifications

Perfluoropropane has a minimum purity of 99.0 mole %.

Uses

Perfluoropropane is useful for high-voltage insulation and as a refrigerant when combined with chlorofluoro hydrocarbons.

Toxicity (2)

Preliminary toxicological examination indicates perfluoropropane to be nontoxic.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Leak Detection

Leaks of perfluoropropane in lines or equipment may be detected by painting the suspected sites with soap water solution; leaks will be indicated by bubble formation.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-C.

Materials of Construction

Since perfluoropropane is a noncorrosive gas, any common or commercially available metal may be used. However, piping systems or vessels to contain perfluoropropane should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

Perfluoropropane is shipped in DOT approved steel cylinders. Cylinders of perfluoropropane are equipped with valves having Compressed Gas Association (CGA) valve outlet No. 660 which has a thread size of 1.030 inches diameter, right-hand external threads, with a flat seat using a washer as a seal (see Figure 1). Lecture bottles have a special $^5/_{16}$ inch-32 threads per inch, female outlet and a $^9/_{16}$ inch-18 threads per inch, male dual valve outlet.

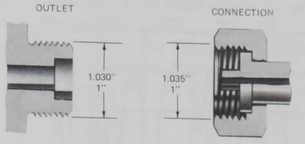


Fig. 1. CONNECTION 660 1.030"-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders of perfluoropropane have safety devices of fusible metal plugs, melting at about 73.9 °C (165 °F).

Recommended Controls

Automatic Pressure Regulators

Matheson regulator Model 1P-660 is recommended for use with perfluoropropane. This regulator has a brass body, brass internal parts, a diaphragm of neoprene rubber, and a neoprene seat. It has a delivery pressure range of 28–240 kPa (4–35 psig). For low pressure regulation, Matheson supplies a Model 70 regulator, which is constructed of an aluminum body and a Buna N diaphragm, and with an oversized pancake body to allow sensitive and accurate low pressure control. Three pressure ranges are available.

Low Pressure Regulator

Model No.	Delivery Pressure Range kPa)	mbar (g)	psig
70B-660	0.5–3.0	5–30	2–12 inches water column
70-660	3.4–34.5	34–345	0.5–5.0 psig
70A-660	34.5–68.9	345–689	5–10 psig

Regulator Model 3321 is recommended for use with lecture bottles.

Manual Controls

Manual needle valve Model 50-660 is available for direct attachment to the cylinder valve outlet. This valve can be equipped with a variety of outlets, such as a hose connection, ¼" tube fitting, or ¼" NPT male or female pipe. It should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. Matheson needle valve Model 31B is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Perfluoropropane is classified by the DOT as nonflammable compressed gas and is shipped with the required "Green Label".

Chemical Preparation

Perfluoropropane has been obtained by a catalyzed reaction between fluorine and carbon and by the electrofluorination of various organic compounds.

Chemical Properties

Perfluoropropane is essentially chemically unreactive. Perfluoropropane is thermally stable as shown by the negligible corrosion or decomposition of perfluoropropane in contact with glass, silicon steel, mild steel, and silicone-glass laminate over a period of 6 months at about 280 °C.

Thermodynamic and Detailed Physical Data

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous perfluoropropane.

Vapor Pressure (3) @ 293.15 °K 767.040 kPa (7.570 1 atm)

For additional vapor pressure data, see Table 1 and Figure 3.

The experimental data (4) are represented by the following equation:

$$\log_{10} P = 16.995\,3 - \frac{1\,435.89}{T} + 0.002\,824\,92T - 4.882\,8\log_{10} T$$

in which P = atm and T = °K.

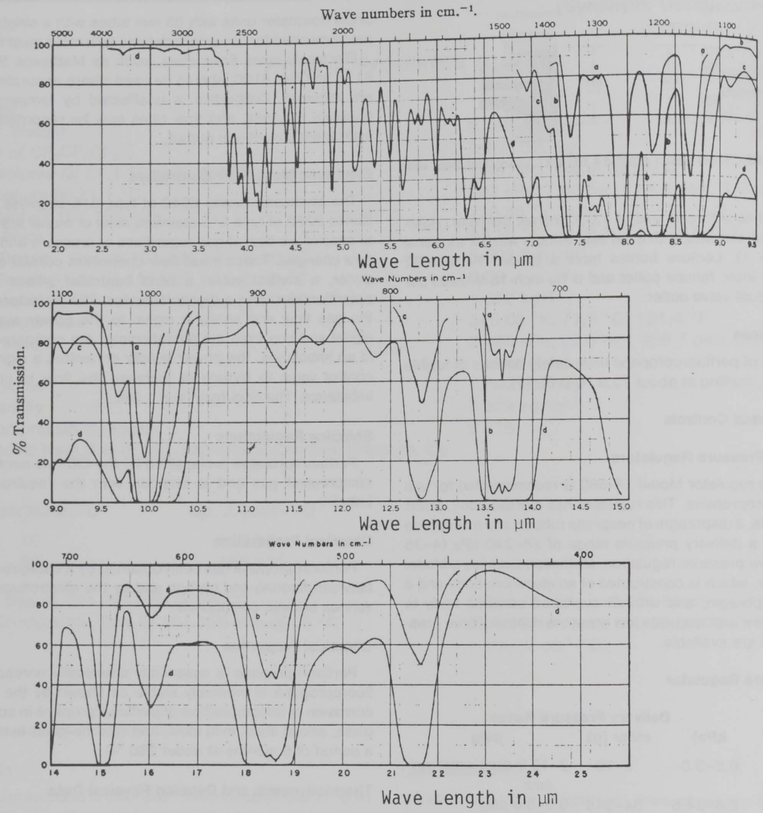


Fig. 2. Infrared spectrum of gaseous perfluoropropane; 10-cm cell, with NaCl and KBr prisms; cell pressure: curve a: 0.200 kPa (1.5 mmHg); curve b: 3.333 kPa (25 mmHg); curve c: 13.332 kPa (100 mmHg); curve d: 66.661 kPa (500 mmHg); temperature: 298.15 °K (25.0 °C) (5).

Latent Heat of Vaporization, ΔHv (3) @ 236.45 °K — 19.619 kJ/mol; 4.689 kcal/mol

For ΔHv values at other temperatures, see Table 1.

Thermodynamic Data

Heat Capacity, Ideal Gas, C_p° @ 25 °C — 147.70 J/(mol·°K)

For the thermodynamic properties of saturated and superheated perfluoropropane, see Tables 1 and 2, respectively.

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of perfluoropropane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, 1977, pp. 119–123, Matheson, Lyndhurst, New Jersey.

[3] F. Fank and J. Joffe, *J. Chem. Eng. Data* 11, 376–379 (1966).

[4] J. A. Brown, *J. Chem. Eng. Data* 8, 106 (1963).

[5] W. F. Edgell, H. D. Mallary, and D. G. Weiblen, *J. Amer. Chem. Soc.* 72, 4856–4859 (1950).

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED PERFLUOROPROPANE (3)

Temperature		kPa Pressure		Entropy J/(mol·°K)		Enthalpy kJ/mol		Latent Heat of Vaporization kJ/kg	Specific Volume dm^3/kg		Density kg/dm^3	
°K	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
173.15	−148.0	1.854	0.018 3	−125.383	−0.000	−21.711	0.000	21.711	0.525 4	4 115.8	1.903	0.000 24
183.15	−130.0	4.266	0.042 1	−119.665	−1.116	−20.685	1.029	21.714	0.543 1	1 887.1	1.841	0.000 53
193.15	−112.0	8.937	0.088 2	−113.181	−1.586	−19.470	2.087	21.557	0.559 7	945.8	1.787	0.001 06
203.15	−94.0	17.316	0.170 9	−105.377	−1.544	−17.924	3.170	21.094	0.575 4	510.2	1.738	0.001 96
213.15	−76.0	31.360	0.309 5	−97.984	−1.081	−16.383	4.273	20.656	0.590 5	293.1	1.693	0.003 41
223.15	−58.0	53.611	0.529 1	−91.208	−0.282	−14.901	5.389	20.290	0.605 1	177.5	1.653	0.005 63
233.15	−40.0	87.200	0.860 6	−84.109	+0.783	−13.278	6.516	19.794	0.619 1	112.4	1.614	0.008 90
243.15	−22.0	135.826	1.340 5	−77.171	2.062	−11.620	7.646	19.266	0.634 7	78.89	1.576	0.012 68
253.15	−4.0	203.704	2.010 4	−70.056	3.504	−9.847	8.776	18.623	0.650 7	50.18	1.537	0.019 93
263.15	+14.0	295.555	2.916 9	−62.989	5.067	−8.010	9.899	17.909	0.668 2	35.00	1.497	0.028 57
273.15	32.0	416.436	4.109 6	−55.896	6.714	−6.092	11.009	17.101	0.688 2	24.97	1.453	0.040 05
283.15	50.0	571.726	5.642 5	−48.705	8.403	−4.073	12.098	16.171	0.711 6	18.14	1.405	0.055 13
293.15	68.0	767.040	7.570 1	−41.421	10.088	−1.947	13.154	15.101	0.742 5	13.36	1.347	0.074 85
303.15	86.0	1 008.093	9.949 1	−34.005	11.713	+0.298	14.158	13.860	0.774 0	9.924	1.292	0.100 77
313.15	104.0	1 300.709	12.837	−26.394	13.189	2.688	15.083	12.395	0.817 2	7.393	1.224	0.135 26
323.15	122.0	1 650.686	16.291	−18.531	14.371	5.245	15.882	10.637	0.872 6	5.473	1.146	0.182 72
333.15	140.0	2 063.686	20.367	−10.276	14.933	8.025	16.423	8.398	0.945 4	3.950	1.058	0.253 16
343.15	158.0	2 545.487	25.122	−2.815	13.817	11.066	16.339	5.273	1.044 4	2.622	0.957	0.381 39
345.05	161.4	2 680.046	26.450	+11.083	11.083	14.117	14.117	0.000	1.590 3	1.590 3	0.628 8	0.628 81

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED PERFLUOROPROPANE (3)

H, ENTHALPY, KJ/MOL; **S**, ENTROPY, J/(MOL·°K); **V**, SPECIFIC VOLUME, DM^3/KG

Pressure kPa	Pressure atm		Temperature, °K 243.15	253.15	263.15	273.15	293.15	313.15	333.15	353.15	373.15	398.15	423.15	448.15	473.15	523.15	573.15
101.325	1	H	7.788 1	9.151 2	10.540 8	11.957 5	14.872 0	17.895 4	21.025 0	24.257 2	27.587 6	31.882 5	36.314 2	40.873 5	45.551 2	55.224 6	65.266 6
		S	4.944 2	10.438 2	15.821 4	21.103 7	31.399 7	41.374 3	51.059 9	60.480 6	69.653 1	80.790 9	91.584 8	102.052	112.207	131.635	149.963
		V	100.9	105.9	110.8	115.6	125.0	134.2	143.3	152.3	161.3	172.4	183.5	194.6	205.6	227.7	249.6
202.650	2	H		8.780 1	10.219 0	11.675 5	14.651 1	17.717 6	20.878 2	24.133 3	27.481 8	31.792 5	36.236 4	40.805 3	45.490 1	55.174 0	65.224 0
		S		3.564 4	9.137 9	14.570 8	25.082 2	35.197 9	44.980 5	54.468 6	63.689 3	74.869 8	85.693 3	96.181 8	106.353	125.803	144.145
		V		50.46	53.20	55.84	60.92	65.80	70.56	75.22	79.83	85.52	91.17	96.78	102.4	113.5	124.6
506.625	5	H					13.915 6	17.142 3	20.412 5	23.745 9	27.152 1	31.516 0	35.998 7	40.596 9	45.304 4	55.022 1	65.095 5
		S					15.572 0	26.128 6	36.341 4	46.057 9	55.438 0	66.755 7	77.673 9	88.230 1	98.451 2	117.969	136.354
		V					22.32	24.68	26.86	28.94	30.95	33.38	35.76	38.11	40.43	45.02	49.55
1 013.250	10	H						15.973 3	19.523.8	23.033 8	26.560 4	31.029 8	35.586 6	40.239 2	44.988 9	54.766 5	64.881 3
		S						17.575 7	28.568 4	38.799 9	48.512 6	60.104 8	71.204 1	81.885 9	92.197 4	111.836	130.297
		V							12.16	13.44	14.61	15.98	17.29	18.55	19.79	22.20	24.55
1 519.875	15	H							18.398 3	22.204 5	25.902 3	30.506 8	35.153 1	39.868 9	44.665 4	54.508 3	64.667 1
		S							22.532 1	33.630 2	43.815 3	55.759 3	67.076 2	77.903 2	88.317 5	108.087	126.628
		V							7.07	8.18	9.12	10.16	11.12	12.03	12.91	14.60	16.23
2 026.500	20	H							16.628 5	21.184 0	25.154 2	29.940 7	34.696 2	39.485 2	44.334 5	54.248 5	64.453 7
		S							15.639 8	28.934 9	39.873 9	52.290 4	63.874 2	74.869 3	85.398 0	105.312	123.938
		V							4.15	5.45	6.33	7.23	8.04	8.78	9.48	10.81	12.08
2 533.125	25	H								19.769 8	24.279 8	29.324 0	34.214 7	39.088 6	43.996 4	53.987 4	64.241 6
		S								23.716 6	36.149 3	49.238 1	61.152 1	72.342 2	82.999 3	103.067	121.783
		V								3.65	4.61	5.47	6.18	6.83	7.42	8.54	9.59
3 039.750	30	H								16.790 8	23.216 6	28.649 1	33.708 0	38.680 2	43.653 3	53.726 3	64.031 1
		S								14.512 1	32.284 6	46.385 5	58.710 3	70.127 6	80.925 3	101.159	119.967
		V								2.01	3.42	4.28	4.95	5.53	6.06	7.04	7.94
3 546.375	35	H									21.875 2	27.910 6	33.178 2	38.262 3	43.306 1	53.466 1	63.823 2
		S									27.936 6	43.613 1	56.448 9	68.122 1	79.074 3	99.484 6	118.388
		V									2.53	3.43	4.07	4.61	5.09	5.97	6.77
4 053.000	40	H									20.261 4	27.114 0	32.628 9	37.836 7	42.957 5	53.207 9	63.618 1
		S									23.056 4	40.870 1	54.310 0	66.269 5	77.388 5	97.980 9	116.983
		V									1.87	2.80	3.42	3.93	4.37	5.17	5.89

Matheson®

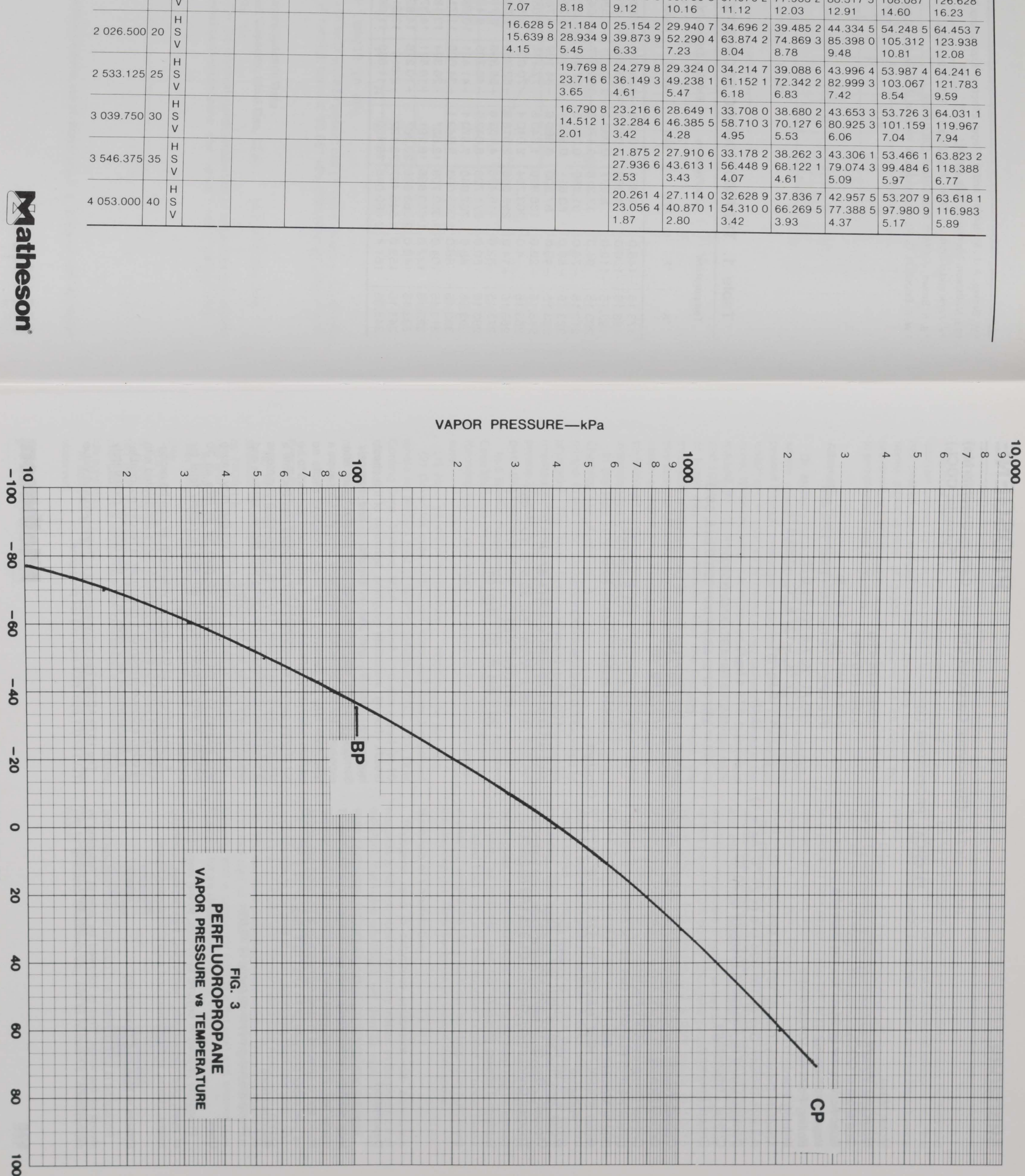


FIG. 3
PERFLUOROPROPANE
VAPOR PRESSURE vs TEMPERATURE

PHOSGENE

(Synonyms: Carbonyl Chloride; Carbon Oxychloride)
(Formula: $COCl_2$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.098 916 4 kg
One Mole of $COCl_2$	0.098 916 4 kg
Specific Volume @ 21.1 °C, 101.325 kPa	243.5 dm^3/kg; 3.9 ft^3/lb
Vapor Pressure @ 21.1 °C	175 kPa; 1.75 bar; 25.4 psia; 1.73 atm
Boiling Point @ 101.325 kPa	280.71 °K; 7.6 °C; 45.6 °F
Melting Point	145.37 °K; −127.8 °C; −198.0 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	4.119 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	3.48
Density, Liquid @ Saturation Pressure @ 20 °C	1.371 4 kg/l
Critical Temperature	455.15 °K; 182.0 °C; 359.6 °F
Critical Pressure	5 674 kPa; 56.74 bar; 823.0 psia; 56.0 atm
Critical Volume	1.921 dm^3/kg
Critical Density	0.521 kg/dm^3
Critical Compressibility Factor	0.285
Latent Heat of Fusion @ 145.37 °K	5.738.4 J/mol; 1 371.5 cal/mol
Dipole Moment, Gas	3.936×10^{-30} C.m; 1.18 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	57.693 J/(mol·°K)
Molar Specific Heat, Liquid @ 270 °K	100.58 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.011 57 mPa·s; 0.011 57 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.008 7 W/(m·°K); 20.8×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 16.7 °C	20.1 mN·m; 20.1 dyn/cm

Description

At ordinary temperatures and pressures, phosgene is a colorless, nonflammable, highly toxic gas with an odor like that of musty hay. It is readily liquefied to a colorless to light yellow liquid and is shipped in steel cylinders as a liquefied gas under its own vapor pressure of 74 kPa (10.7 psig) at 21.1 °C.

Specifications

Phosgene has a minimum purity of 99.0%.

Uses

Phosgene is used in organic synthesis, in the manufacture of dyes, pharmaceuticals, herbicides, insecticides, synthetic foams, resins, and polymers and as a chlorinating agent.

Effects in Man and Toxicity (2)

Phosgene is a lung irritant and causes severe damage to the alveoli of the lungs. This is followed by edema, resulting in asphyxiation. Inhalation of the gas produces catching of the breath, choking, immediate coughing, tightness of the chest, lacrimation, difficulty and pain in breathing, and cyanosis. Serious symptoms may not develop until several hours after exposure, for the immediate symptoms produced by even a fatal dose may be relatively mild since phosgene elicits no marked respiratory reflexes; thus, a person who appears to be but slightly gassed immediately after exposure may become a casualty several hours later. The most pronounced symptoms of phosgene poisoning are coughing with bloody sputum and weakness which may last for months.

An atmosphere containing 20 ppm by volume may cause lung injuries in 2 minutes, even 25 ppm for as little as 30 minutes is very dangerous, and 90 ppm is rapidly fatal for exposures of 30 minutes or less.

A concentration of 0.5 ppm by volume in air can be recognized by the sense of smell by normal persons acquainted with its odor; a concentration of 1 ppm in air is readily noticeable; at a concentration of 2 ppm in air, the odor is moderately strong.

The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 0.1 ppm (0.4 mg/m^3) for phosgene.

First Aid Treatment (2)

Remove the victim to an uncontaminated atmosphere. Administer oxygen by mask, if the person is breathing; if breathing has ceased, give artificial respiration, preferably with simultaneous administration of oxygen. Observe 24–48 hours for premonitory signs of pulmonary edema. Subsequent treatment is symptomatic and supportive.

Alternative Suggestions for Medical Treatment (3)

Dr. McNally (3) recommends placing the victim in a hospital where oxygen inhalations can be given, the oxygen being passed through ammonium carbonate (2 grams 1½ ounces of water) and introduced by means of two catheters placed in the nose. When the lungs are highly edematous or if cyanosis is marked, the victim should be given an ampule of Salyrgan daily and 100 ml of a 50% glucose solution intravenously, or 500 ml of blood may be withdrawn. After the first few hours, the inhalation of oxygen may be given by the tent method. During this time the victim should be kept at absolute rest. The application of external heat is important. The irritating cough may be lessened by the administration of dilaudid or codeine. Treat symptomatically, giving digitalis to strengthen the heart.

In the May 1970 issue of Accident Case Histories of the Chemical Manufacturers' Association, case No. 1658 is reported. In this case, six persons were accidentally exposed to phosgene. Five were treated with hexamethylenetetramine (methenamine) and urotropine and they recovered. The sixth person claimed he had not smelled phosgene and was not given this treatment. Several hours later he died.

In a special supplement to the May 1970 issue of Accident Case Histories of the Chemical Manufacturers' Association, the following first aid procedure is suggested for phosgene exposure:

(1) Have patient in flat position . . . head may be elevated.

(2) Cover his eyes with a wet towel and have the patient inhale an aerosol mist of methylpolysiloxane (XEC 151, Dow Corning Corp., Midland, Mich., diluted 1:10 with water) for 10 minutes.

(3) Wait 15 minutes and repeat. This is repeated 4 consecutive times, which gives 40 minutes total of silicone spray.

(4) Inhale oxygen, if necessary.

Precautions in Handling and Storage

(a) Personnel handling and using phosgene should have available for immediate use gas masks of a design approved by NIOSH for phosgene service with approved canisters for use with phosgene.

Additional gas masks should be located in convenient places near where the phosgene is being used, for use in emergencies.

(b) Phosgene should be used only in forced ventilation areas or preferably in hoods with forced ventilation. Phosgene emitted from equipment in high concentrations should be discharged into a scrubbing tower containing 5% sodium hydroxide solution.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection (4)

Leaks of phosgene in lines and equipment may be detected by holding a bottle of concentrated aqueous ammonia near the suspected sites (white fumes will appear) and by the following tests:

(a) Dissolve 0.25 g p-nitroso-m-dimethylaminophenol (prepared by nitrosating m-diethylaminophenol) in 50 ml benzene (soln. A); dissolve 0.20 g m-diethylaminophenol in 50 ml benzene soln. B). Mix equal parts of solutions A and B and apply to a piece of filter paper. Exposure of this paper to phosgene changes the color from brown to green. The sensitivity to phosgene is 0.2 ppm. Solution A is somewhat unstable and must be renewed every 3–4 months.

(b) Dissolve 5 g of p-dimethylaminobenzaldehyde and 5 g of colorless diphenylamine each in 50 ml carbon tetrachloride and mix. Dip filter papers immediately into this solution and dry. Store the papers in tightly sealed brown bottles. Exposure of this paper to 0.5 ppm of phosgene produces a light lemon yellow color in 4–5 minutes and a dark yellow in 10–15 minutes. Higher concentrations produce proportionately greater color changes up to a dark orange shade, which occurs in about 8 minutes for 2 ppm, and in 15 minutes with 1 ppm.

Matheson supplies a Toxic Gas Detector System, Model No. 8014K, for detection of phosgene in air. The Model 146 (0.05–50 ppm) detector tube contains a chemical reagent which absorbs and reacts with phosgene. A color stain is produced which varies in length according to the concentration being measured. The length of the stain is measured against a calibration chart which is furnished with each detector.

In the event of a leak around the cylinder valve that cannot be stopped, it is recommended that the cylinder cap be affixed as tightly as possible, and the cylinders placed in a well-ventilated cool spot and the supplier notified at once. Leaks appearing around the valve stem can be stopped by tightening the packing nut. Turn clockwise as viewed from above.

Materials of Construction

Phosgene used in anhydrous equipment with anhydrous reagents is not corrosive to ordinary metals. In the presence of moisture, corrosive conditions will develop rapidly, in which case monel, tantalum or glass-lined equipment may be used.

Piping and vessels to contain phosgene should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

Phosgene is shipped in DOT approved steel cylinders. Cylinders are equipped with Compressed Gas Association (CGA) No. 660 stainless steel diaphragm valves. The valve outlet has a thread size of 1.030″ in diameter with right-hand external threads, with a connector having a flat seat and washer (see Figure 1 for an illustration).

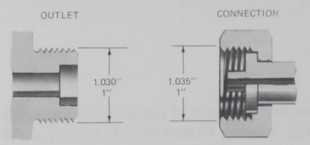


Fig.1. CONNECTION 660 1.030″-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders of phosgene are not equipped with safety devices. They should, therefore, be stored away from sources of heat to avoid dangerous hydrostatic pressures from developing within the cylinder.

Recommended Controls

Manual Controls

Matheson needle valve Model 55A-660 of monel is recommended for use to remove gaseous or liquid phosgene.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Phosgene is classified by DOT as a "Class A" poison and is shipped under the required "Poison Gas Label."

Commercial Preparation

Phosgene is prepared by passing a mixture of carbon monoxide and chlorine over activated carbon.

Chemical Properties

Phosgene is readily hydrolyzed by water to carbonic acid and hydrochloric acid and on ammonolysis forms urea. With equimolar quantities of amines, phosgene initially forms carbamoyl chlorides, which lose hydrogen chloride on heating to give isocyanates. With an excess of amine, phosgene forms urea derivates. Depending on the reaction conditions and the ratio of reactants, alcohols when treated with phosgene yield first chloroformates and then carbonates.

Thermodynamic and Detailed Physical Data

Molecular Structure (5)

Phosgene is a planar molecule, with C_{2v} point group symmetry and a symmetry number of two. The structural parameters are as follows: interatomic distances: C═O 1.166 Å (1.166×10^{-10} m); Cl—O 2.589 Å (2.589×10^{-10} m); Cl—Cl 2.884 Å (2.884×10^{-10} m); C—Cl 1.746 Å (1.746×10^{-10} m); bond angle: 111.3°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous phosgene.

Vapor Pressure

The vapor pressure from 215.531 °K to 281.153 °K as determined experimentally (6) is shown below.

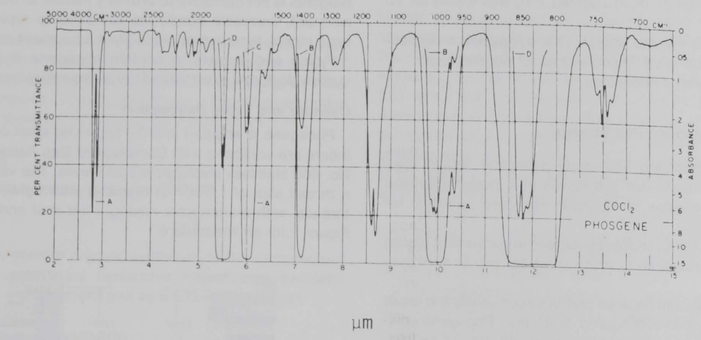


Fig. 2. Infrared spectrum of gaseous phosgene; 10-cm path length cell, with NaCl optics; cell pressure: curve A: 94.659 kPa (710 mmHg); curve B: 10.666 kPa (80 mmHg); curve C: 2.266 kPa (17 mmHg); curve D: 0.133 kPa (1 mmHg) (8).

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
215.531	3.300	33.0	24.75
221.459	4.976	49.8	37.32
227.367	7.289	72.9	54.67
233.793	10.766	108	80.75
241.018	16.281	163	122.12
247.623	23.182	232	173.88
255.372	34.064	341	255.50
264.063	50.913	509	381.88
272.197	72.165	722	541.28
277.098	88.002	880	660.07
281.153	103.074	1 031	773.12

These data are represented by the following vapor pressure equation:

$$\log_{10} p = 9.680\,20 - \frac{1\,690.3}{T} - 7.898 \times 10^{-3} T + 5.584\,7 \times 10^{-6} T^2$$

in which p = cmHg and T = °K.

Vapor pressure values at higher temperatures are shown below (7).

Temperature, °K	Vapor Pressure kPa	bar	atm
283.15	109.431	1.09	1.08
293.15	157.054	1.57	1.55
303.15	219.875	2.20	2.17
313.15	300.935	3.01	2.97
323.15	404.287	4.04	3.99
333.15	531.956	5.32	5.25
343.15	690.023	6.90	6.81
353.15	879.501	8.80	8.68

Temperature, °K	Vapor Pressure kPa	bar	atm
363.15	1 108.496	11.1	10.94
373.15	1 378.020	13.8	13.6
383.15	1 692.128	16.9	16.7
393.15	2 056.898	20.6	20.3
403.15	2 472.330	24.7	24.4
413.15	2 948.558	29.5	29.1
423.15	3 485.580	34.9	34.4
433.15	4 093.530	40.9	40.4
443.15	4 762.275	47.6	47.0
453.15	5 512.080	55.1	54.4
455.15*	5 674.200*	56.7*	56*

* Critical Points.

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/mol
250.15	25.945
280.71	24.401
300.15	23.330

Thermodynamic Properties of Phosgene As Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	57.697 J/(mol·°K)
Entropy, S°	283.742 J/(mol·°K)
Free Energy of Function, $(F^\circ_{298} - H^\circ_{298})/298$	−283.742 J/(mol·°K)
Enthalpy Difference, $H^\circ_{298} - H^\circ_0$	12.866 kJ/mol
Enthalpy of Formation, ΔH°_f	−220.078 kJ/mol
Free Energy of Formation, ΔF°_f	−205.941 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of phosgene, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 134–138, Matheson, Lyndhurst, New Jersey.

[3] W. D. McNally, *Toxicology, 1937*, pp. 419–429, Industrial Medicine, Chicago, Illinois.

[4] M. B. Jacobs, *The Analytical Toxicology of Industrial Inorganic Poisons, 1967*, pp. 649–651, John Wiley & Sons, Inc., New York, New York.

[5] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[6] W. F. Giauque and W. M. Jones, *J. Amer. Chem. Soc.* 70, 120–124 (1948).

[7] *International Critical Tables*, Volume 3, p. 237.

[8] R. H. Pierson, A. N. Ffetcher, and E. St. Clair Gantz, *Anal. Chem.* 28, 1218 (1956).

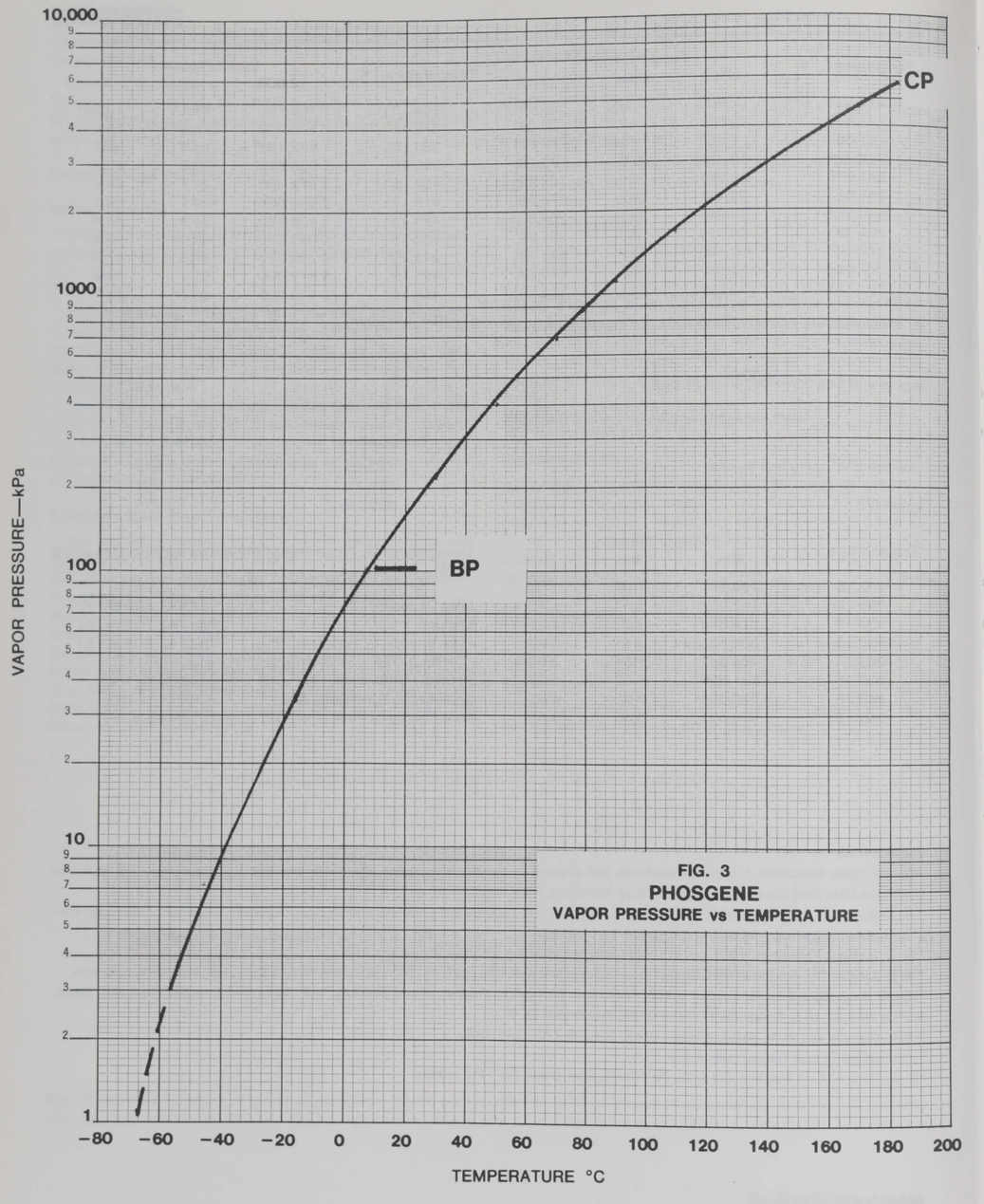


FIG. 3
PHOSGENE
VAPOR PRESSURE vs TEMPERATURE

PHOSPHINE

(Formula: PH_3)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.033 997 8 kg
One Mole of PH_3	0.033 997 8 kg
Specific Volume @ 21.1 °C, 101.325 kPa	711.7 dm^3/kg; 11.4 ft^3/lb
Vapor Pressure @ 20 °C	4 190 kPa; 41.9 bar; 607.4 psia; 41.3 atm
Boiling Point @ 101.325 kPa	185.415 °K; −87.7 °C; −125.9 °F
Triple Point	139.37 °K; −133.8 °C; −208.8 °F
Absolute Density @ 101.325 kPa @ 25 °C	1.402 4 kg/m^3
Relative Density @ 101.325 kPa @ 25 °C (Air = 1)	1.184
Density, Liquid @ Saturation Pressure @ −87.7 °C	0.744 kg/l
Critical Temperature	324.75 °K; 51.6 °C; 124.9 °F
Critical Pressure	6 535 kPa; 65.35 bar; 947.9 psia; 64.5 atm
Critical Volume	3.324 dm^3/kg
Critical Density	0.301 kg/dm^3
Critical Compressibility Factor	0.274
Latent Heat of Fusion @ −133.8 °C	1.130 kJ/mol; 270 cal/mol
Dipole Moment, Gas	1.935×10^{-30} C·m; 0.58 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	37.126 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 0 °C	0.010 0 mPa·s; 0.010 0 cP
Viscosity, Liquid @ −75.0 °C	0.180 mPa·s; 0.180 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	$0.016\ 3$ W/(m·°K); 39.0×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −125.0 °C	25.5 mN/m; 25.5 dyn/cm
Solubility In Water @ 101.325 kPa @ 17 °C	26 cm^3/100 ml water
Refractive Index, Gas @ 101.325 kPa, n_D @ 25 °C	1.000 800

Description

At room temperature and atmospheric pressure, phosphine is a colorless, flammable, highly toxic gas with an odor of decaying fish. It is shipped as a liquefied gas in steel cylinders under its own vapor pressure of 4 086 kPa (592 psig) at 21.1 °C.

Specifications

Matheson supplies an Electronic Grade phosphine with a minimum purity of 99.999% (excluding hydrogen).

Effects in Man and Toxicity (2)

The symptoms exhibited by phosphine poisoning are faintness, weakness, apathy, nausea, vomiting, dyspnea, fall in blood pressure, change in pulse rate, diarrhea, intense thirst, oppressed feeling in the chest, convulsions, paralysis, coma.

A concentration of 2000 ppm is lethal to man in a few minutes. Concentrations of 400–600 ppm are dangerous to life after exposures for 30–60 minutes. The maximum concentration tolerated for exposures of 60 minutes is in the range 100–190 ppm. The maximum concentration that can be tolerated without symptoms for several hours is 7 ppm. The minimum warning concentration is 1.4–2.8 ppm.

In low concentrations, phosphine does not appear to be a hemolytic agent, but it may cause hyperemia, especially in the lungs, kidneys, and brain. Chronic phosphorus poisoning may result from the decomposition of phosphine in the body.

The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 0.3 ppm (0.4 mg/m^3) for phosphine.

First Aid Treatment (2)

Remove the victim promptly to an uncontaminated atmosphere. Keep the victim warm (not hot) and quiet. Administer pure oxygen. If breathing is weak and has stopped, give artificial respiration with simultaneous administration of oxygen.

Suggestions for Medical Treatment

Use intermittent positive pressure oxygen for pulmonary edema. If muscle spasm or muscle tremor is present, use barbiturates to prevent convulsions. Treat anemia, if severe, by transfusion. Treatment otherwise is symptomatic and supportive.

Precautions in Handling and Storage

Phosphine is hazardous because of its high toxicity and flammability. Phosphine should be used in a well-ventilated area, preferably in a hood with forced ventilation. Personnel handling and using phosphine should have available for immediate use, oxygen generating gas masks of a type approved by NIOSH, or self-contained breathing apparatus. Additional gas masks should be located in convenient areas near where the phosphine is being used, in case of emergency. Do not store reserve stocks of phosphine with cylinders containing oxygen or other highly oxidizing or flammable materials. Ground all lines and equipment used with phosphine.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Never use a flame to detect phosphine leaks. Soapy water, painted over the suspected area, will indicate leaks by the formation of bubbles. It is preferable that the system be pretested for leaks with nitrogen.

Analytical Detection

Several methods are described for the detection and determination of phosphine. It may be detected by the brown to black color produced by phosphine on filter paper wetted with silver nitrate solution. It may be estimated by trapping the gas in bromine water or sodium hydrochlorite solution, and, after elimination of the bromine, determination of the phosphate present. It may be determined rapidly in gases by use of the reaction $PH_3 + 3HgCl_2 \rightarrow P(HgCl)_3 + 3HCl$, the quantity of acid being proportional to the volume of phosphine present.[2]

Matheson supplies an Arsine/Phosphine Monitor Model 8040 for parts-per-billion detection of phosphine in air at the TLV (300 ppb). The Model 8040 Monitor utilizes a chemically-treated tape located between a light source and a photo cell. Ambient air is continuously drawn across the tape by an integral low pressure vacuum pump. Phosphine darkens the tape, changing the photocell output. When the tape darkens to a preset level, the built-in alarm sounds continuously until the monitor is reset.

Matheson also supplies a Toxic Gas Detector Model 8014K for detection of high range (Model 121 SC: 50–700 ppm) and low range (Model 121 SD: 0.25–10 ppm) concentrations, respectively, of phosphine. The detector tube contains a chemical reagent which absorbs and reacts with phosphine. A color stain is produced which varies in length with the concentration being measured. The phosphine concentration is then read directly off the scale on the detector tube.

Disposal of Leaking Cylinders

Don appropriate gas mask and remove cylinder to a hood. Attach appropriate regulator or needle valve having a long flexible hose to the cylinder valve outlet. Introduce the gas at a moderate rate into an excess of sodium or calcium hypochlorite solution. The phosphine is oxidized to phosphate. The solution is sent to the plant disposal unit for disposal. Tag the cylinder as defective and return the cylinder to the supplier according to the supplier's instructions.

Materials of Construction

Piping and accessories leading to equipment for the thermal decomposition of phosphine may be of iron or steel construction and should be adequately designed to withstand pressures to be encountered.

Cylinder and Valve Description

Pure phosphine is shipped in DOT approved cylinders. The cylinder valve outlet is a Compressed Gas Association (CGA) 660 which is 1.030″ right-hand external thread sealing on a flat seat by the use of a gasket. Figure 1 shows the standard valve outlet and mating connection. Cylinders containing dopant mixtures of phosphine in UHP background gas are supplied with CGA No. 350 cylinder valve outlet.

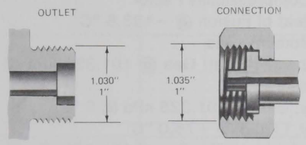


Fig. 1 CONNECTION 660 1.030″-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders containing phosphine are not equipped with safety devices. They should, therefore, be stored away from sources of heat to avoid the development of dangerous pressures within the cylinder.

Recommended Controls

Automatic Pressure Regulators

Matheson supplies single stage regulator Model 3502-660 for use with phosphine. Matheson also supplies a two stage regulator, Model 3800-660, for use with phosphine.

The Model 3502 regulator has a type 316 stainless steel body, stainless steel diaphragm, internal parts of stainless steel, a Tefzel seat, Teflon gaskets, and a diaphragm packless outlet valve (Model 4374) with ¼″ Gyrolok tube fitting. It has a delivery pressure range of 0–170 kPa (0–25 psig).

The Model 3800 regulator has a type 316 stainless steel body and diaphragm, a Tefzel seat, Kel-F and Teflon gaskets, and a diaphragm packless outlet valve (Model 4374) with ¼″ Gyrolok tube fitting. It has a delivery pressure range of 28–620 kPa (4–90 psig).

Both regulators can be supplied with a helium leak rate certification.

Regulator Model 3503-350 is recommended for use with phosphine gas mixtures, which are supplied in cylinders with CGA valve outlet connection No. 350. The regulator has a stainless steel diaphragm and a delivery pressure range of 0–25 psig.

Manual controls should be used only where manual flow control is needed and should not be used as pressure controls since they will not prevent pressure from building up if a system becomes clogged or if a system itself is closed.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electric mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Phosphine is classified by the DOT as a "Class A" poison and flammable gas. It is shipped under required "Poison Gas Label" and "Red Gas Label."

Chemical Preparation

Phosphine is prepared by hydrolysis of phosphides, by the reaction of white phosphorous with alkali, by disproportionation of phosphorous or hypophosphorous acid, or by direct combination of the elements under pressure.

Chemical Properties

Phosphine is a much weaker base than ammonia. It forms phosphonium halides with the appropriate hydrogen halide. Phosphine is a stronger reducing agent than ammonia. It burns readily in air and, with oxygen, it explodes. Phosphine begins to decompose into its elements at about 375 °C. It reacts spontaneously with chlorine.

Thermodynamic and Detailed Physical Data

Molecular Structure

Phosphine is a pyramidal molecule, having C_{3v} point group symmetry and a symmetry number of three (3). The P—H bond distance is 1.420 02 ± 0.000 06 Å (1.420 02 ± 0.000 06 × 10^{-10} m), and the H—P—H bond angle is 93.345 4 ± 0.004 3° (4).

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous phosphine.

Vapor Pressure (5)

The vapor pressure of liquid phosphine from 136.30 °K to 199.46 °K is represented by the following Antoine vapor pressure equation:

$$\log_{10} p = A - \frac{B}{C + t} \quad \text{or} \quad t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.715 59, 645.512, and 256.066, respectively.

Some calculated values are shown below.

Temperature, °K	Vapor Pressure		
	kPa	mbar	mmHg
136.30	2.666	26.7	20
143.32	5.333	53.3	40
147.82	7.999	80.0	60
151.22	10.666	107	80
153.97	13.332	133	100
163.307	26.664	267	200
169.382	39.997	400	300
174.008	53.329	533	400
177.794	66.661	667	500
181.026	79.993	800	600
183.862	93.325	933	700
185.415	101.325	1 013.25	760
186.399	106.658	1 067	800
188.70	119.990	1 200	900
190.81	133.322	1 333	1 000
194.60	159.986	1 600	1 200
199.46	199.983	2 000	1 500

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/mol
173.15	16.643
185.415	14.598
198.15	14.225

Thermodynamic Properties of Phosphine As Ideal Gas @ 25 °C (3)

Heat Capacity, C_p°	37.104 J/(mol·°K)
Entropy, S°	210.196 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−210.196 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	10.138 kJ/mol
Enthalpy of Formation, ΔH_f°	22.886 kJ/mol
Free Energy of Formation, ΔF_f°	25.409 kJ/mol

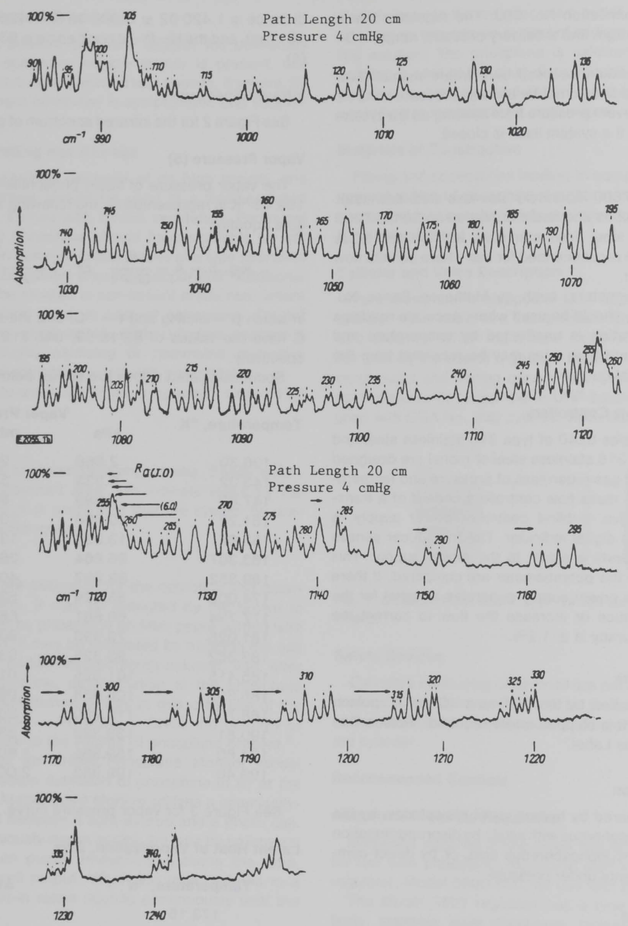


Fig. 2. Infrared spectrum of gaseous phosphine in the region 880–1 240 cm^{-1}. Three sets of measurements were made on each of the numbers above the absorption lines shown on Figure 2, which were tabulated, analyzed, and discussed (6).

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of phosphine, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 69–72, Matheson, Lyndhurst, New Jersey.

[3] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U.S. Government Printing Office, Washington, D. C.

[4] A. G. Maki, R. L. Sams, and W. B. Olson, *J. Chem. Phys.* 58, 4502–4512 (1973).

[5] B. J. Zwolinski *et al.*, *Selected Values of Properties of Chemical Compounds, 1968*, Volume 1, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[6] J. M. Hoffman, H. H. Nielsen, and K. N. Rao, *Z. Elektrochem.* 64, 606–616 (1960).

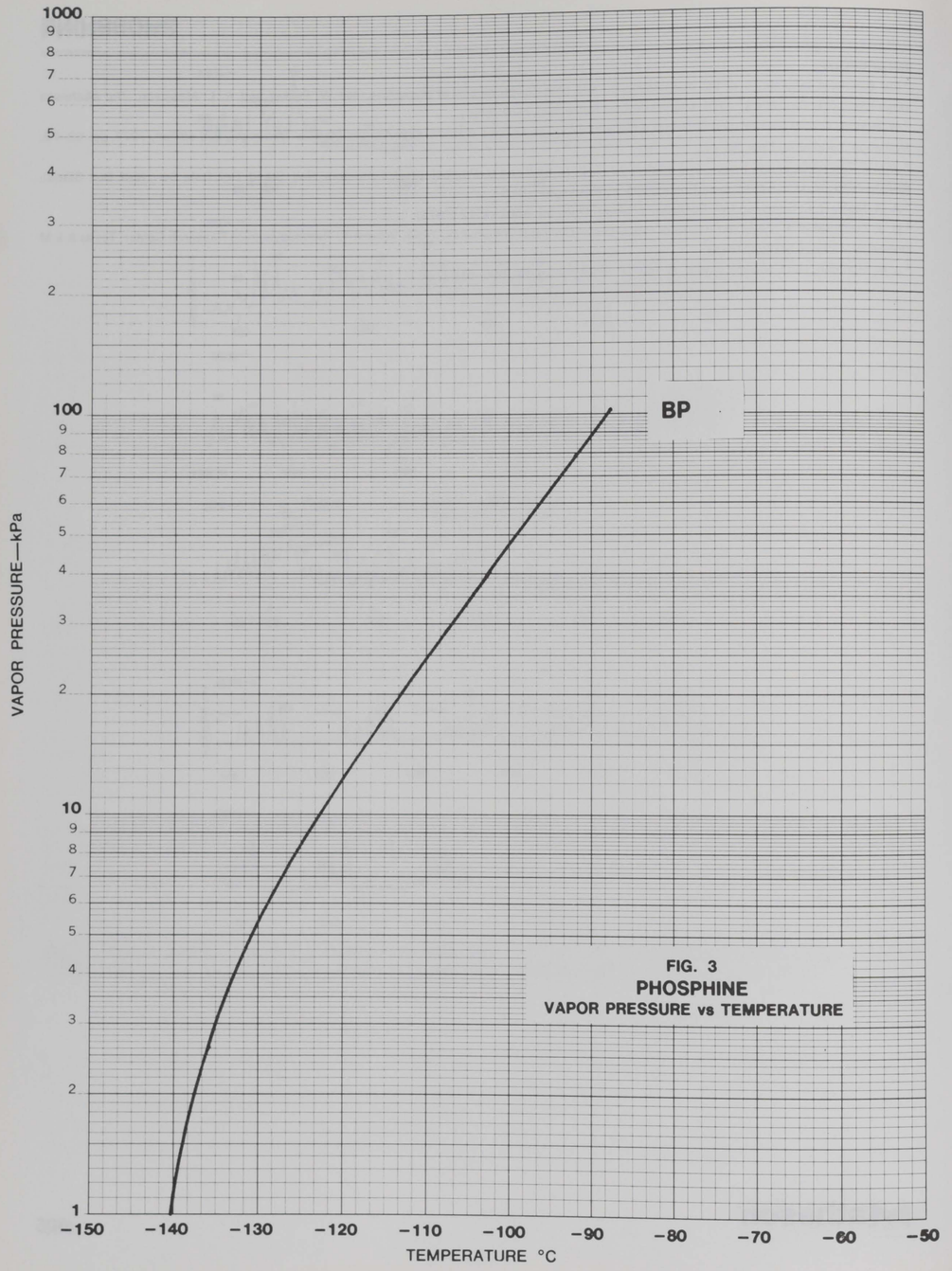


FIG. 3
PHOSPHINE
VAPOR PRESSURE vs TEMPERATURE

PHOSPHORUS PENTAFLUORIDE

(Formula: PF_5)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.125 966 kg
One Mole of PF_5	0.125 966 kg
Specific Volume @ 21.1 °C, 101.325 kPa	193.5 dm^3/kg; 3.1 ft^3/lb
Vapor Pressure @ 21.1 °C	2 860 kPa; 28.6 bar; 414.7 psia; 28.2 atm
Boiling Point @ 101.325 kPa	188.65 °K; −84.5 °C; −120.1 °F
Freezing Point	179.35 °K; −93.8 °C; −136.8 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	5.372 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	4.46
Density, Liquid @ Saturation Pressure @ −84.5 °C	1.636 kg/l
Critical Temperature	292.10 °K; 19.0 °C; 66.1 °F
Critical Pressure	3 394 kPa; 33.94 bar; 492.3 psia; 33.5 atm
Critical Volume	1.604 dm^3/kg
Critical Density	0.624 kg/dm^3
Critical Compressibility Factor	0.282
Latent Heat of Fusion @ −93.8 °C	12.104 kJ/mol; 96.1 kJ/kg
Dipole Moment, Gas	0 C·m
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	83.958 J/(mol·°K)
Refractive Index, Gas @ 101.325 kPa, n_D @ 25 °C	1.000 587 8
Trouton Constant	21.79
Dielectric Constant, Gas	1.002 063

Description

At room temperature and atmospheric pressure, phosphorus pentafluoride is a colorless, strongly fuming gas with an irritating odor. It is shipped as a liquified gas in size 7X cylinders at a pressure of 2 760 kPa (400 psig) at 21.1 °C, and in size 4X cylinders at the same pressure. It is hydrolyzed by water yielding phosphoric acid with oxyfluorophosphates as intermediates depending on the pH.

Effects in Man and Toxicity

Since phosphorus pentafluoride is a gas which is readily hydrolyzed by moisture, the effects produced and its toxicity would be similar to those described in this Data Book under hydrogen fluoride.

First Aid Suggestions

The first aid procedures to be followed are similar to those described under hydrogen fluoride in this Data Book.

Precautions in Handling and Storage

Phosphorus pentafluoride should be handled in a well-ventilated area, preferably a hood with forced ventilation. Workers who handle the gas should wear a NIOSH-approved gas mask for acid gases or one with an independent oxygen or air supply. Additional self-contained breathing equipment should be located in areas not likely to be contaminated, for use in emergencies. Workers who handle the gas should be provided with a full face mask and/or chemical safety goggles and neoprene rubber gloves. Adequate emergency showers and eye-wash fountains should be located in convenient areas. Introduction of phosphorus pentafluoride below the surface of a liquid (water, alcohols, ethers, and other compounds) may create a hazard owing to the possibility of suckback into the cylinder. This should be guarded against by the use of traps or check valves. Equipment used for phosphorus pentafluoride should not be used with other gases, particularly oxygen, since the gas may have oil vapors which will coat out on equipment and may cause fires when combined with oxygen under pressure.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Equipment to contain phosphorus pentafluoride should be pretested for leaks with dry air. Small leaks of phosphorus pentafluoride may be detected with a flash or squeeze bottle of aqueous ammonia (formation of dense white fumes).

Cylinder valve leaks can usually be corrected by tightening the valve packing nut (turn clockwise as viewed from above).

Disposal of Leaking Cylinders

Leaking cylinders of phosphorus pentafluoride which cannot be readily corrected may be disposed of by the procedure described in Appendix I-D.

Materials of Construction

Materials of construction recommended for the handling of dry phosphorus pentafluoride are steel, nickel, monel, and the more noble metals. Pyrex glass is also suitable up to about 250 °C for the dry gas. Saran, hard rubber and paraffin wax are recommended for handling moist gas.

Cylinder and Valve Description

Phosphorus pentafluoride is shipped in DOT approved, high pressure steel cylinders. Cylinders are equipped with Compressed Gas Association (CGA) connection No. 330. This cylinder valve outlet has a thread size of 0.825 inch diameter, with left-hand external threads, with a flat seal, using a washer to seal (see Figure 1).

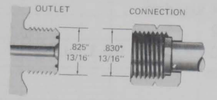


Fig. 1. CONNECTION 330 .825"-14 LH EXT. used with Flat Seat and Washer

Safety Devices

Cylinders of phosphorus pentafluoride are equipped with safety devices which consist of platinum-plated frangible discs (bursting at about 22 750 kPa (3 000 psig)) backed up with fusible metal plugs, melting at 71.1 °C (160 °F).

Recommended Controls

Automatic Pressure Regulators

Matheson has the following corrosion resistant, single stage regulators available for use with phosphorus pentafluoride.

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
B15A-330	28–345	0.28–3.45	4–50
B16A-330	345–4 480	3.45–44.8	50–650

These regulators have chemically deposited pure nickel on brass bodies, chemically deposited pure nickel on nickel-silver alloy diaphragms, Kel-F seats, and internal parts and outlet needle valves of monel. A monel check valve (Model 402V) is recommended for use with these regulators to prevent suck-back of foreign materials into the regulators.

Manual Controls

Matheson needle valve Model 55-330 is available for direct attachment to the cylinder valve outlet. These needle valves are of monel bar stock. and may be equipped with a variety of outlets (¼" tube fitting or ¼" NPT male or female pipe), but are usually supplied with hose connections.

They should be used only where manual flow control is needed and should not be used as a pressure control since they will not prevent pressure from building up if a system becomes clogged or if the system itself is closed.

A Model 60L needle valve is available for lecture bottles.

Flowmeters

Matheson Series 7600 laboratory monel flowmeter units with 150 mm tubes and floats are recommended for use where definite flow rates must be known.

Monel electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8260 of monel is designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Phosphorus pentafluoride is classified by the DOT as a nonflammable compressed gas and is shipped under the required "Green Label".

Chemical Preparation

Phosphorus pentafluoride has been prepared by several methods:

1. By the reaction of phosphorus pentachloride with arsenic trifluoride (violent reaction).
2. By addition of fluorine to phosphorus trifluoride; and
3. By heating phosphorus trifluoride with chlorine and bromine in a mole ratio of 5:3 at temperatures of at least 250 °C.
4. By the reaction of calcium fluoride with phosphorus pentoxide.
5. By the reaction of arsenic trifluoride with phosphorus pentachloride.

Chemical Properties

Phosphorus pentafluoride is thermally stable, as indicated by its low rate of decomposition in an electric spark. Phosphorus pentafluoride does not attack dry glass even at 250 °C. Slight traces of moisture hydrolyze phosphorus pentafluoride to phosphorus oxyfluoride and hydrogen fluoride. With more water, phosphorus pentafluoride ultimately yields phosphoric acid. Phosphorus pentafluoride is a somewhat milder Lewis acid than boron trifluoride. Phosphorus pentafluoride exhibits the same general acceptor properties as boron trifluoride, but the complexes formed with nitrogen and oxygen bases are much less stable than the analogous boron trifluoride complexes. Phosphorus pentafluoride does not react with hydrogen, oxygen, phosphorus, sulfur or iodine. Active metals reduce phosphorus pentafluoride to phosphorus trifluoride and phosphorus at elevated temperatures.

Thermodynamic and Detailed Physical Data

Molecular Structure (2)

Phosphorus pentafluoride has a trigonal bipyramidal structure. It has D_{3h} point group symmetry and a symmetry number of six. The structural parameters are as follows: bond distances: P-Feq (eq = equatorial) 1.534 Å (1.534×10^{-10} m); P-F_{ax} (ax = axial) 1.577 Å (1.577×10^{-10} m); bond angles: Feq-P-Feq 120°; Feq-P-F_{ax} 74.3°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of the ν_3 band and Figure 3 for the infrared spectrum of ν_4 and ν_6 bands.

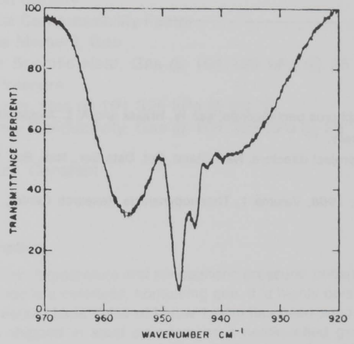


Fig. 2. Infrared band (946.6 cm^{-1}) due to the ν_3 vibrational mode of gaseous phosphorus fluoride; 10-cm path length cell, with AgCl windows; cell pressure: 0.267 kPa (2 mmHg) (4).

Vapor Pressure (3)

The vapor pressure of liquid phosphorus pentafluoride between 174.05 °K and 199.46 °K is represented by the following Antoine vapor pressure equation:

$$\log_{10} p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.914 4, 647.21, and 245.0, respectively.

Some calculated values are shown below.

Temperature, °K	Vapor Pressure		
	kPa	mbar	mmHg
174.05	39.997	400	300
178.65	53.329	533	400
181.65	66.661	667	500
184.65	79.993	800	600
187.15	93.325	933	700
188.65	101.325	1 013.25	760
189.45	106.658	1 067	800
191.55	119.990	1 200	900
193.45	133.322	1 333	1 000
196.95	159.986	1 600	1 200
201.25	199.983	2 000	1 500

Latent Heat of Vaporization @ 188.65 °K	17.196 kJ/mol; 4.110 kcal/mol

Thermodynamic Properties of Phosphorus Pentafluoride As Ideal Gas @ 25 °C (2)

Heat Capacity, C_p°	84.835 J/(mol·°K)
Entropy, S°	300.696 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−300.696 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	16.527 kJ/mol
Enthalpy of Formation, ΔH_f°	−1 576.950 kJ/mol
Free Energy of Formation, ΔF_f°1	−1 508.713 kJ/mol

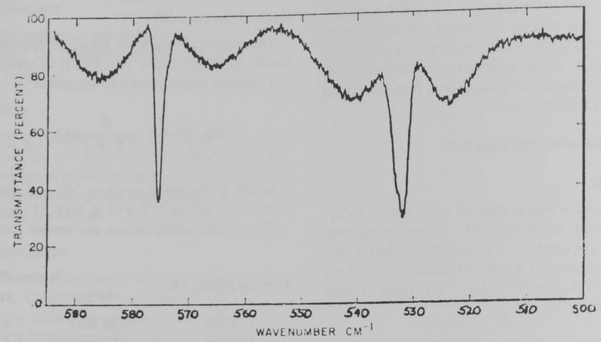


Fig. 3. Infrared band (575.1 cm^{-1}) due to the ν_4 vibrational mode and infrared band (532.5 cm^{-1}) due to the ν_6 vibrational mode of gaseous phosphorus pentafluoride; 10-cm path length cell, with AgCl windows; cell pressure: 0.400 kPa (3 mmHg) (4).

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of phosphorus pentafluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. NSRD-NBS 37, U. S. Government Printing Office, Washington, D. C.

[3] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds, 1968*, Volume 1, Thermodynamcis Research Center, Texas A & M University, College Station, Texas.

[4] L. C. Hoskins and R. C. Lord. *J. Chem. Phys.* 46, 2402–2412 (1967).

PHOSPHORUS TRIFLUORIDE

(Synonym: Phosphorus (III) Fluoride)
(Formula: PF_3)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.087 969 kg
One Mole of PF_3	0.087 969 kg
Specific Volume @ 21.1 °C, 101.325 kPa	274.7 dm^3/kg; 4.4 ft^3/lb
Vapor Pressure @ 21.1 °C	6 838 kPa; 68.38 bar; 991.7 psia; 67.48 atm
Boiling Point @ 101.325 kPa	171.95 °K; −101.2 °C; −150.2 °F
Melting Point	121.85 °K; −151.3 °C; −240.3 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	3.590 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	3.03
Density, Liquid @ Saturation Pressure @ 171.95 °K	1.574 kg/l
Critical Temperature	271.10 °K; −2.0 °C; 28.3 °F
Critical Pressure	4 326 kPa; 43.26 bar; 627.4 psia; 42.69 atm
Critical Volume	1.688 dm^3/kg
Critical Density	0.592 kg/dm^3
Critical Compressibility Factor	0.285
Dipole Moment, Gas	3.526×10^{-30} C·m; 1.03 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	58.693 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.018 71 mPa·s; 0.018 71 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.016 4 W/(m·°K) 39.2 $\times 10^{-6}$ cal·cm/(s·cm^2·°C)
Trouton Constant	20.3

Description

At room temperature and atmospheric pressure, phosphorus trifluoride is a colorless, nonfuming gas. It is highly poisonous [a Threshold Limit Value of below 1 ppm has been suggested] . It is shipped in steel cylinders as a nonliquefied gas, the cylinder pressure being 6 740 kPa (977 psig) at 21.1 °C.

Specifications

Phosphorus trifluoride has a minimum purity of 99 mole %. Small amounts of chlorine-containing gases may be present as impurities.

Uses

Phosphorus trifluoride is used for fluorination of certain metals at elevated temperatures and to prepare mixed halides related to phosphorus trifluoride.

Toxicity

Phosphorus trifluoride is a highly poisonous gas. Inhalation of the vapor causes difficulty in breathing, chest pains, and nausea. A Threshold Limit Value (TLV) of below 1 ppm is suggested for phosphorus trifluoride (concentration in air to which nearly all workers may be exposed, day after day, without adverse affects).

First Aid Suggestions

Summon a physician at once for any person who has been exposed to phosphorus trifluoride. Prior to the physician's arrival, first aid measures should be taken. Those presented herein are based on what is believed to be common practice in industry. Their adoption in any specific case should be subject to prior endorsement by a competent medical advisor.

Inhalation

Administer 100% oxygen at once.

Eye Contact

Wash eyes immediately with copious amounts of water for a minimum of 15 minutes, while holding the eyelids apart to insure contact of water with all the tissues of the surface of the eyes and lids. An eye specialist should be contacted at once.

Skin Contact

Wash at once with copious amounts of water for at least 15 minutes.

Precautions in Handling and Storage

Phosphorus trifluoride should be handled in a well-ventilated area, preferably a hood with forced ventilation. Workers who

handle the gas should wear a NIOSH-approved gas mask for acid gases or one with an independent oxygen or air supply. Additional self-contained breathing equipment should be located in areas not likely to be contaminated, for use in emergencies. Workers who handle the gas should be provided with a full face shield and/or chemical safety goggles and neoprene rubber gloves. Adequate emergency showers and eye-wash fountains should be located in convenient areas. Use check valves or traps when introducing phosphorus trifluoride below the surface of a liquid. Do not use equipment used with phosphorus trifluoride with other gases, particularly oxygen.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Equipment to contain phosphorus trifluoride should be pretested with dry nitrogen. Leaks which develop subsequently may be detected by painting the suspected sites with soap water solution; leaks will be indicated by bubble formation.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-D.

Materials of Construction

The dry gas may be handled in steel, nickel, monel, and the more noble metals. Pyrex glass is also suitable for handling the dry gas at ambient temperature.

Cylinder and Valve Description

Phosphorus trifluoride is shipped in DOT approved, high pressure steel cylinders. Cylinders are equipped with Compressed Gas Association (CGA) connection No. 330. This cylinder valve outlet has a thread size of 0.825 inch diameter, with left-hand external threads, with a flat seal, using a washer to seal (see Figure 1).

Lecture bottles have a special 5/16 inch-32 threads per inch female outlet.

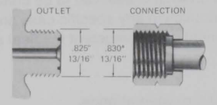


Fig. 1 CONNECTION 330 .825″-14 LH EXT. used with Flat Seat and Washer

Safety Devices

Cylinders of phosphorus trifluoride are equipped with safety devices which consist of platinum-plated frangible discs (bursting at about 22 750 kPa (3 300 psig) backed up with fusible metal plugs, melting at 71.1 °C (160 °F).

Recommended Controls

Automatic Pressure Regulators

Matheson has the following corrosion resistant, single stage regulators available for use with phosphorus trifluoride.

Model No.	Delivery Pressure Range kPa	bar (g)	psig
B15B-330	28–345	0.28–3.45	4–50
B16B-330	345–4 480	3.45–44.8	50–650

A monel check valve (Model 402V) is recommended for use with these regulators to prevent suckback on foreign materials into the regulators.

Manual Controls

Matheson needle valve Model 55-330 is available for direct attachment to the cylinder valve outlet. These needle valves are of monel bar stock, and may be equipped with a variety of outlets (¼″ tube fitting or ¼″ NPT male or female pipe), but are usually supplied with hose connections.

They should be used only where manual flow control is needed and should not be used as a pressure control since they will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. A Model 60L needle valve is available for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory monel flowmeter units with 150 mm tubes and floats are recommended for use where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8260 of monel is designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Phosphorus trifluoride is classified by the DOT as a nonflammable compressed gas and is shipped under the required "Green Label".

Chemical Preparation

Phosphorus trifluoride has been prepared by several methods:

1. By halogen exchange between phosphorus trichloride and hydrogen fluoride.
2. By reaction of phosphorus trichloride with arsenic trifluoride lead fluoride, antimony trifluoride, or zinc fluoride.
3. By reaction of phosphorus tribromide with zinc fluoride.
4. By thermal reaction of the mixed phosphorus halide, PF_3Cl_2, with hydrogen, mercury, aluminum, tin, lead, iron, nickel, or phosphorus.

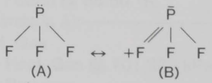
Chemical Properties

Phosphorus trifluoride is hydrolyzed only slowly by water at room temperature, rapidly by aqueous base. It reacts with dry ammonia to form a solid addition product of unknown structure. Aqueous solutions of chromic acid, potassium permanganate, or bromine oxidize phosphorus trifluoride rapidly. Alcohols react with phosphorus trifluoride to give alkyl phosphites. Hot metals react with phosphorus trifluoride to give phosphides and fluorides. Phosphorus trifluoride reacts with fluorine, chlorine, and bromine to give PF_5, PF_3Cl_2, and PF_3Br_2, respectively, the latter however tends to disproportionate: $5PF_3Br_2 \rightarrow 3PF_5 + 2PBr_5$. The donor and acceptor properties of phosphorus trifluoride are discussed in Reference (2).

Thermodynamic and Detailed Physical Data

Molecular Structure

The phosphorus trifluoride molecule has a pyramidal structure (A) which amounts to a tetrahedron in which an electron pair occupies one position. There is also evidence for an appreciable amount of multiple bonding (3), leading to consideration of structure B. The structural parameters are as follows (4): P—F bond distance: 1.570 Å (1.570 × 10^{-10} m); F····F distance 2.364 3 Å (2.364 3 × 10^{-10} m); F—P—F bond angle: 97.8°.



Phosphorus trifluoride has C_{3v} point group symmetry and a symmetry number of three (4).

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous phosphorus trifluoride.

Vapor Pressure (5)

The vapor pressure of liquid phosphorus trifluoride between 122.15 °K and 184.85 °K is represented by the following Antoine vapor pressure equation:

$$\log_{10} p = A - \frac{B}{C + t} \text{ or } t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and T = °K, and the constants A, B, and C have the values of 6.860 4, 620.22, and 257.0, respectively.

Some calculated values are shown below:

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
122.15	1.333	13.3	10
128.15	2.666	26.7	20
134.15	5.333	52.3	40
138.15	7.999	80.0	60
141.25	10.666	107	80
143.75	13.322	133	100
152.15	26.644	266	200
157.65	39.997	400	300
161.75	53.329	533	400
165.15	66.661	667	500
168.05	79.993	800	600
170.65	93.325	933	700
171.95	101.325	1 013.25	760
172.85	106.658	1 067	800
174.95	119.990	1 200	90
176.85	133.322	1 333	1 000
180.15	159.986	1 600	1 200
184.45	199.983	2 000	1 500

Latent Heat of Vaporization @ 171.95 °K 14.598 kJ/mol; 3.489 kcal/mol

Thermodynamic Properties of Phosphorus Trifluoride As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	58.689 J/(mol·°K)
Entropy, S°	272.935 J/(mol·°K)
Free Energy Function, ($F^\circ_{298} - H^\circ_{298}/298$	−272.935 J/(mol·°K)
Enthalpy Difference, $H^\circ_{298} - H^\circ_0$	12.937 kJ/mol
Enthalpy of Formation, ΔH_f°	−940.981
Free Energy of Formation, ΔF_f°	−924.907

PHOSPHORUS TRIFLUORIDE

Matheson

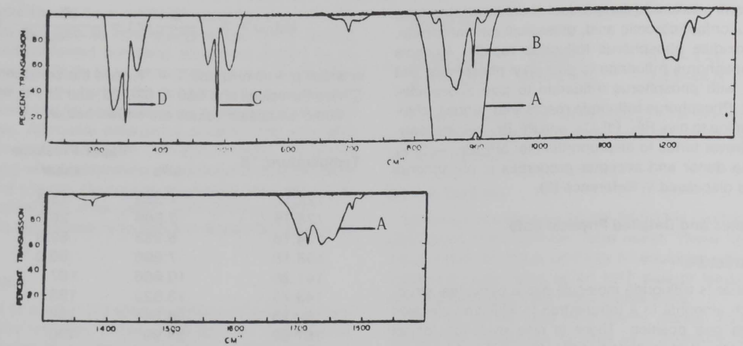


Fig. 2. Infrared absorption spectrum of gaseous phosphorus trifluoride; 10-cm gas cell, with KBr or polythene windows; cell pressure: curve A: 46.663 kPa (350 mmHg); curve B: 0.267 kPa (2 mmHg); curve C: 3.333 kPa (25 mmHg); curve D: 9.999 kPa (75 mmHg) (6).

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of phosphorus trifluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] R. Schmutzler, in *Advances in Fluorine Chemistry*, M. Stacey, J. C. Tatlow, and A. G. Sharpe, editors, Volume 5, *1965*, pp. 55–60, Butterworth, Inc., Washington, D. C.

[3] P. Kisliuk, *J. Chem. Phys.* 22, 86 (1954).

[4] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[5] B. J. Zwolinski, *et al.*, *Selected Values of Properties of Chemical Compounds, 1968*, Volume 1, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[6] M. K. Wilson and S. R. Polo, *J. Chem. Phys.* 20, 1716–1719 (1952).

Matheson

PROPANE

(Synonym: Dimethylmethane)
(Formula: $CH_3CH_2CH_3$ or C_3H_8)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.044 097 kg
One Mole of C_3H_8	0.044 097 kg
Specific Volume @ 21.1 °C, 161.325 kPa	530.6 dm^3/kg; 8.5 ft^3/lb
Vapor Pressure @ 21.1 °C	853 kPa; 8.53 bar; 123.7 psia; 8.42 atm
Boiling Point @ 101.325 kPa	231.09 °K; −42.1 °C; −43.7 °F
Triple Point	85.44 °K; −187.7 °C; −305.9 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	1.868 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	1.55
Density, Liquid @ Saturation Pressure @ 20 °C	0.500 5 kg/l
Critical Temperature	369.99 °K; 96.8 °C; 206.3 °F
Critical Pressure	4 266 kPa; 42.66 bar; 618.7 psia; 42.10 atm
Critical Volume	4.438 dm^3/kg
Critical Density	0.225 kg/dm^3
Critical Compressibility Factor	0.271
Latent Heat of Fusion @ 85.50 °K	3.534 kJ/mol; 19.1 kcal/kg
Flammability Limits in Air	2.2–9.5% (by volume)
Dipole Moment, Gas	28×10^{-30} C.m; 0.084 D
Molar Specific Heat, Gas @ 101.325 kPa @ 26.8 °C	
@ Constant Pressure	74.01 J/(mol·°K)
@ Constant Volume	64.81 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 26.8 °C, Cp/Cv	1.142
Molar Specific Heat, Liquid @ 25 °C	111.13 J/(mol·°K); 26.56 cal/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.007 90 mPa·s; 0.007 90 cP
Viscosity, Liquid @ −40 °C	0.22 mPa·s; 0.22 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.016 74 W/(m·°K); 40.0×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −40 °C	0.148 5 W/(m·°K); 354.9×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −40 °C	15.3 mN/m; 15.3 dyn/cm
Solubility In Water @ 101.325 kPa @ 18 °C	6.5 cm^3/0.1 kg water
Dielectric Constant @ 0 °C	1.61
Autoignition Temperature	741 °K; 468 °C; 874 °F
Flash Point	169.15 °K; −104.0 °C; −155.2 °F
Refractive Index, Liquid @ Saturation Pressure @ 20 °C	1.289 8
Heat of Combustion, Gas @ 25 °C and Constant Pressure	
Gross, to form H_2O(liq) + CO_2(gas)	2 220.03 kJ/mol; 530.60 kcal/mol
Net, to form H_2O(gas) + CO_2(gas)	2 044.01 kJ/mol; 488.53 kcal/mol
Heat of Combustion, Liquid @ 25 °C and Constant pressure	
Gross, to form H_2O(liq) + CO_2(gas)	2 203.42 kJ/mol; 526.63 kcal/mol
Net, to form H_2O(gas) + CO_2(gas)	2 027.40 kJ/mol; 484.56 kcal/mol

Description

At room temperature and atmospheric pressure, propane is a colorless, flammable, nontoxic gas, with a characteristic natural gas odor. Propane is one of the group of liquefied petroleum gases. It is normally shipped in low pressure cylinders as a liquefied compressed gas under its own vapor pressure of 752 kPa (109 psig) at 21.1 °C.

Matheson

Specifications

Matheson supplies four grades of propane, the specifications of which are given below:

1. Research Purity Grade

This grade of propane is of the highest purity that is available. The minimum purity of the liquid phase is 99.99 mol %.

2. Instrument Purity Grade

This grade of propane has a minimum purity of 99.5 mol % in the liquid phase. There is essentially no air in the liquid phase. Special precautions are taken to eliminate traces of water, oil, and nonvolatile matter.

3. C.P. Grade

This grade has a minimum purity of 99 mol % in the liquid phase.

4. Natural Grade

This grade has totally saturated 96 mol % or better hydrocarbon propane and 4 mol % or less butane and lighter fractions in the liquid phase.

Uses

Propane is widely used as a fuel for suburban home heating systems and gas appliances. Propane is also used as a fuel for intraplant trucking where gasoline fumes are considered to be obnoxious. It is also used as a refrigerant gas and as a thermobulb fill for temperature and pressure control instruments. It has been used as a low temperature extraction solvent. It has been used extensively as a refrigerant in chemical, petroleum refining, and gas processing operations, and as a selective solvent for removing asphaltic components from the higher-boiling fractions of crude oils.

Effects In Man and Toxicity (2)

Apart from methane and ethane which are simple asphyxiants and cyclopropane which is a general anesthetic, the hydrocarbon propane has some degree of anesthetic action and is mildly irritating to the mucous membranes and/or acts as a simple asphyxiant. Thus, depending on the concentration and time of exposure, symptoms such as rapid respiration, air hunger, diminished mental alertness, muscular incoordination, faulty judgment, emotional instability, rapid fatigue, nausea, vomiting, prostration, and loss of consciousness, convulsions, and finally deep coma and death may occur.

Contact of the liquid form of propane with the skin can cause frostbite. Symptoms of frostbite are the change of skin from pink to white or grayish-yellow, pain which quickly subsides, and a cold and numb feeling.

Propane has a low order of inhalation toxicity. Brief exposures to 10 000 ppm (1%) cause no symptoms in man. Its odor is not detectable below 20 000 ppm (2%).

The 1979 ACGIH has classified propane as a simple asphyxiant.

First Aid Treatment (2)

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration and oxygen simultaneously. Treat symptomatically thereafter.

Skin Contact

In case of skin contact with liquid propane, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise toe affected part while it is being warmed.

Precautions in Handling and Storage

The hazards due to the handling of propane stem mainly from its extreme flammability. Store and use propane cylinders in well-ventilated areas away from heat and all ignition sources such as flames and sparks. Never use flames to detect flammable gas leaks, use soapy water solution. Do not use propane around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of propane cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all lines and equipment used with propane.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

All fittings and joints should be painted with soap solution to detect leaks, which will be indicated by bubble formation. Never use a flame to detect leaks.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-A.

Materials of Construction

Since propane is a noncorrosive gas any common or commerically available metal may be used. However, piping systems or vessels to contain propane should be designed to have a working pressure as specified by competent engineers using a safety factor conforming to the A.S.M.E. code for pressure piping.

Cylinder and Valve Description

DOT approved cylinders containing propane are usually of the low pressure type having a rated service pressure of 1 034 kPa (150 psig) or more. Cylinders of propane are equipped with valves having Compressed Gas Association (CGA) valve outlet No. 510 having a thread size of 0.885 inch diameter-14 threads per inch, left-hand internal threads accepting a bullet-shaped nipple. See Figure 1 for illustration of the valve outlet and mating connection. This valve outlet is standard for all liquefied petroleum gases. Valves used in this service by Matheson are of the diaphragm type and contain no packing. They are therefore relatively leak-free and require no packing adjustments. Lecture bottles have a special $^{5}/_{16}$"-32 threads per inch, female outlet and a $^{9}/_{16}$"-18 threads per inch, male dual valve outlet.

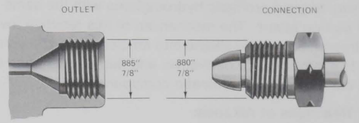


Fig. 1. CONNECTION 510 .885"-14 LH EXT. accepting a Bullet Shaped Nipple

Safety Devices

A number of different safety devices are permitted on cylinders containing propane. A frangible disc is allowed in cylinders having a minimum required test pressure of 20 680 kPa (3 000 psig) or higher, and is required in only one end of the container. A 73.9 °C (165 °F) fusible metal may be used; however, when cylinders are over 30 inches long, exclusive of the neck, this device is required in both ends. A frangible disc backed up with 73.9 °C (165 °F) fusible metal is permitted in cylinders having a minimum required test pressure of 20 680 kPa (3 000 psig) or higher and when cylinders are over 30 inches long, exclusive of the neck, this device is required at both ends. The most commonly used safety device, which is employed by Matheson, is the spring-loaded safety relief valve. If cylinder pressure becomes dangerously high, usually due to overheating, the safety relief device will open (at approximately 2 590 kPa (375 psig)) and release propane gas until the pressure again returns to a safe level.

Recommended Controls

Automatic Pressure Regulators

Matheson supplies single stage regulator Model 1P-510 for use with Instrument Purity Grade, C. P. Grade and Natural Grade propane. This regulator has a brass body, neoprene diaphragm, and neoprene seat. It has a delivery pressure range of 28–240 kPa (4–35 psig). It is equipped with a delivery pressure gauge and needle valve for accurate flow control. No tank gauge is supplied since the vapor pressure of the gas over liquid propane will remain constant as long as any liquid remains in the cylinder; therefore, the pressure is no indication of cylinder content. A tank gauge can be supplied, however, if requested.

For low pressure regulation, Matheson supplies a Model 70 regulator constructed of a forged aluminum body and Buna N diaphragm. This regulator is constructed with an oversize, pancake body to allow sensitive and accurate low pressure control. Three pressure ranges are available as follows:

Model No.	Delivery Pressure Range		
	kPa	mbar (g)	psig
70B-510	0.05–3.0	5–30	2–12 inches water column
70-510	3.4–34.5	34–345	0.5–5.0 psig
70A-510	34.5–68.9	345–689	5–10 psig

This regulator is designed primarily for liquefied petroleum gases where it is particularly suited for fuel gas burner operation, since its steady low pressure delivery permits a stable flame to be obtained.

The Model 71S regulator has an aluminum body, a large diaphragm, Teflon seat, and stainless steel needle valve outlet with ¼" NPT male and hose connection. It has a delivery pressure range of 3.4–40 kPa (0.5–6 psig).

Regulator Model 3321 of brass construction, neoprene diaphragm, and Kel-F seat is recommended for use with lecture bottles of Instrument Purity Grade and C. P. Grade of propane. It has a delivery pressure range of 28–410 kPa (pg) (4–60 psig).

Single stage regulators Model 19S-510 and Model 71S-510 are recommended for use with Research Purity Grade propane. The 19S regulator has a brass body, German silver diaphragm, nylon seat, and aluminum and nylon gaskets, and a diaphragm packless outlet valve with a ¼" Gyrolok tube fitting. It has a delivery pressure range of 0–170 kPa (0–25 psig).

Manual Controls

Matheson needle valve Model 50-510 is a brass bar stock valve that is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a hose connection, ¼" tube fitting, or ¼" NPT male or female pipe. It should be used only where manual flow control is needed and should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. A Model 31B manual needle valve can be supplied for use with lecture bottles, where accurate flow control is desired. This valve is available for use with Instrument Purity, C. P., and Natural Grades of propane.

Manual control Model 4351-510 of diaphragm packless construction and ¼" Gyrolok outlet connection is recommended for use with Research Purity Grade propane.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Propane is classified by the DOT as a flammable compressed gas and is shipped with the required "Red Gas Label".

Commercial Preparation

Propane is a constituent of crude petroleum and natural gas. It is obtained therefrom by refining and processing operations.

Chemical Properties[3]

Propane is a member of the alkane or paraffin series of hydrocarbons. The alkanes as a group are chemically inert substances, not being attacked by cold bromine, sulfuric acid, and nitric acid. However, the alkanes undergo, with a change in conditions, both chlorination and nitration, and, in addition, many thermal reactions, isomerization, dehydrogenation, cyclization, and other reactions. When the alkanes are heated from 500 °C upwards, they undergo complex reactions which may be accelerated or directed by different catalysts to give a variety of products. The following reactions exemplify the different types of reactions which the alkanes undergo and which are of great importance to the petroleum industry. The reactions which may occur simultaneously are: (*a*) dehydrogenation, (*b*) thermal degradation or cracking, (*c*) aromatization.

(a) Dehydrogenation

This reaction is of importance in the petroleum industry for the conversion of ethane, propane, butane, isobutane, and pentanes into olefins wherein higher yields and higher reaction velocities are promoted by catalysts. Industrially the olefins so obtained are polymerized or used for alkylating isoalkanes to produce high grade motor fuel. Ethylene, propylene, and isobutylene are used for the manufacture of a great variety of industrially important aliphatic compounds.

(b) Thermal Degradation or Cracking

The pyrolysis of gaseous, liquid, and solid alkanes at temperatures of about 500–1 000 °C has been widely studied with the object of obtaining lower branched chain alkanes and olefins. Noncatalytic pyrolysis of alkanes at about 1 400–1 600 °C results in more complete degradation to yield the industrially important carbon black, hydrogen, and acetylene. By the use of suitable catalysts, the cracking temperature can be reduced to 200–500 °C, and by careful control of the conditions, the desired products can be obtained in good yields.

(c) Aromatization

The alkane can be converted into aromatic hydrocarbons by high temperature cracking, and by hydroforming (or catalytic reforming). The aromatization of alkanes occurs at a temperature of 500–1 000 °C, most likely by the mechanism of first forming olefins and diolefins which combine to yield cyclic compounds. The latter in the presence of metalic catalysts are dehydrogenated into aromatic compounds. In the hydroforming process, practically quantitative conversion is effected of aliphatic hydrocarbons containing more than six carbon atoms in the chain, to yield aromatic hydrocarbons with the same number of carbon atoms. The mechanism of this reaction involves dehydrogenation of the alkane into an olefin, cyclization of the olefin to a cyclohexane derivative, and dehydrogenation of the cyclic compound to an aromatic compound.

Other Reactions of Alkanes:

(d) Oxidation

Alkanes can be oxidized by atmospheric oxygen at temperatures well below their ignition point. The rate of oxidation of the alkanes in the vapor phase increases with the length of chain, and decreases by chain branching. Methyl groups have a stabilizing effect.

(e) Halogenation

The halogens, except iodine, react readily with alkanes. Little or no halogenation occurs in the dark, but in daylight or ultraviolet light methane and ethane are attacked, except by iodine, with explosive violence. Halogenation of the alkanes may be affected in the liquid or gaseous state with ultraviolet light or heat; catalysts may accelerate the reaction. The formation of isomeric halides and polysubstitution products—and, with chlorine, the danger of explosive reaction—may be minimized by control of concentrations, temperature, and catalysts, and in the case of chlorination, by carrying out the reaction in the liquid phase with carbon dioxide, nitrogen, steam, hydrogen chloride, or chlorinated hydrocarbons as diluents.

(f) Nitration

While alkanes show little or no reactivity towards nitric acid or nitrogen tetroxide at ordinary temperatures, reaction proceeds at temperatures of 100–450 °C in the liquid phase and preferably in the vapor phase to give nitroalkanes.

(g) With Inorganic Reagents

(1) Under ultraviolet light the alkanes react with a mixture of sulfur dioxide and chlorine at room temperature to give sulfonyl chlorides. (2) In the presence of organic peroxides, the alkanes react with sulfuryl chloride in the dark to yield alkyl chloride, sulfur dioxide, and hydrogen chloride. (3) Alkane, e.g., propane, butane, and isobutane, react with sulfur dioxide in the vapor phase yielding sulfonic acids or their anhydrides, sulfones, and sulfates. (4) At about 300 °C, and above, alkanes containing four or more carbon atoms react with sulfur to give olefins, diolefins, and thiophene derivatives. (5) Alkanes, including propane, 3-methylpentane, and heptane react with

Fig. 2. Infrared spectrum of gaseous propane; 10-cm path length cell, with KBr windows; cell pressure: curve A (complete scan): 9.333 kPa (70 mmHg); curve B (partial scan): 1.333 kPa (10 mmHg) (7).

phosphorus trichloride and oxygen at 25 °C to yield alkanephosphonyl chlorides which on hydrolysis give alkylphosphonic acids. (6) In the presence of aluminum chloride, alkanes react with carbon monoxide to give ketones, e.g., isobutane yields methyl isopropyl ketone.

(h) With Organic Reagents

(1) In the presence of actinic light, or in the dark in the presence of organic peroxides, alkanes, e.g., pentane, heptane, and isooctane, react with oxalyl chloride or phosgene to give acid chlorides. (2) Normal alkanes react with acid chlorides in the presence of aluminum chloride to give ketones. (3) Isoalkanes condense with haloalkanes in the presence of Friedel-Crafts catalysts, e.g., isobutane and vinyl chloride in the presence of aluminum chloride yield 1,1-dichloro-3,3-dimethylbutane. (4) Isoalkanes undergo halogen-hydrogen exchange with tertiary or secondary alkyl halides in the presence of aluminum halides. (5) Isoalkanes react with unsaturated aliphatic carboxylic acids in the presence of aluminum chloride to give saturated fatty acids. (6) Tertiary alkanes react with benzoyl peroxide yielding tert-alkyl benzoate, benzene, and carbon dioxide or (if the reaction takes this course) tert-alkylbenzene, benzyl alcohol, and carbon dioxide. (7) Tertiary alkanes and ketones in the presence of sulfuric acid react to give tert-alcohols. (8) Isoalkanes condense with aromatic hydrocarbons in the presence of silica or alumina.

Thermodynamic and Detailed Physical data

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous propane.

Vapor Pressure (Below 101.325 kPa) (4)

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
144.25	0.133	1.33	1
157.75	0.667	6.67	5
164.65	1.333	13.3	10
172.25	2.666	26.7	20
180.75	5.333	53.3	40
186.15	7.999	80.0	60
193.55	13.332	133	100
204.75	26.664	267	200
217.55	53.329	533	400
231.05	101.325	1 013.25	760

Vapor pressures above 101.325 kPa (1 atm) are shown below (5).

Temperature, °K	Vapor Pressure kPa	bar	atm
231.05	101.325	1 013 25	1
247.55	202.650	2.03	2
274.55	506.625	5.07	5
300.05	1 013.250	10.1	10
331.25	2 026.500	20.3	20
351.85	3 039.750	30.4	30
367.95	4 053.000	40.5	40
369.95	4 255.650	42.6	42.0

For additional vapor pressure data, see Table 1 and Figure 3.

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED PROPANE LIQUID AND VAPOR (8)

Temperature		Pressure		Entropy J/(mol·°K)		Enthalpy kJ/mol		Latent Heat of Vaporization kJ/mol	Specific Volume dm³/kg		Density kg/dm³	
°K	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
189.50	−118.57	10.132	0.1	150.147	258.273	14.291	34.788	20.497	1.587 4	37 735	0.630 0	0.000 03
216.54	−69.90	50.662	0.5	164.321	254.008	17.147	36.560	19.413	1.669 0	786.7	0.599 2	0.001 27
231.10	−43.69	101.325	1	170.635	251.834	18.556	37.317	18.761	1.716 7	412.7	0.582 5	0.002 42
248.06	+6.91	202.650	2	177.617	249.910	20.237	38.170	17.933	1.777 9	216.1	0.562 5	0.004 63
259.33	18.18	303.975	3	182.049	248.949	21.370	38.718	17.348	1.821 0	147.7	0.549 1	0.006 77
268.05	26.90	405.300	4	185.436	248.322	22.269	39.128	16.859	1.859 5	112.4	0.537 8	0.008 90
275.24	35.76	506.625	5	188.196	247.862	23.018	39.445	16.427	1.893 6	90.71	0.528 1	0.001 02
281.44	40.29	607.950	6	190.579	247.527	23.682	39.713	16.031	1.925 3	75.92	0.519 4	0.013 17
286.90	56.75	709.275	7	192.670	247.234	24.272	39.930	15.658	1.954 8	65.20	0.511 6	0.015 34
291.83	65.62	810.600	8	194.468	246.942	24.807	40.119	15.312	1.984 3	57.06	0.504 0	0.017 52
296.30	73.67	911.925	9	196.182	246.733	25.313	40.286	14.973	2.011 5	50.59	0.497 1	0.019 77
300.44	81.12	1 013.250	10	197.813	246.524	25.794	40.428	14.634	2.038 7	45.42	0.490 5	0.022 02
317.42	111.69	1 519.815	15	204.377	245.687	27.826	40.934	13.108	2.172 5	29.50	0.460 3	0.033 90
330.70	135.59	2 026.500	20	209.645	244.893	29.628	41.281	11.653	2.304 0	21.23	0.434 0	0.047 10
341.71	155.41	2 533.125	25	214.287	244.182	31.263	41.478	10.215	2.444 6	16.07	0.409 1	0.062 23
351.23	172.54	3 039.750	30	218.635	243.262	32.848	41.498	8.650	2.621 5	12.44	0.381 5	0.080 39
359.61	187.63	3 546.375	35	223.109	241.882	34.428	41.181	6.753	2.877 7	9.565	0.347 5	0.104 55
367.18	201.25	4 053.000	40	228.754	239.123	36.510	40.324	3.814	3.329 0	6.683	0.300 4	0.149 63
370.0	206.33	4 265.782	42.10	234.733	234.733	38.580	38.580	0.000	4.437 9	4.437 9	0.225 3	0.225 33

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/mol
231.05	18.774
298.15	15.083

For additional ΔHv values, see Table 1.

Thermodynamic Data

The thermodynamic properties of saturated propane liquid and vapor and of the superheated vapor are listed in Tables 1 and 2, respectively.

Thermodynamic Properties of Propane As Ideal Gas @ 25 °C (6)

Heat Capacity, C_p°	73.513 J/(mol·°K); 17.57 cal/(mol·°K)
Enthalpy of Formation, ΔH_f°	−103.85 kJ/mol; −24.82 kcal/mol
Free Energy of Formation, ΔF_f°	−23.489 kJ/mol; −5.614 kcal/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of propane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 11–16, Matheson, Lyndhurst, New Jersey.

[3] E. H. Rodd, editor, *Chemistry of Carbon Compounds*, *1951*, 1A, pp. 230–248, Elsevier Publishing Co., New York, New York.

[4] *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p. 3–59, McGraw-Hill Book Company, Inc., New York, New York.

[5] **Ibid.**, p. 3–62.

[6] C. E. Miller and F. D. Rossini, *Physical Constants of hydrocarbons*, C_1 to C_{10}, *1961*, American Petroleum Institute, New York, New York.

[7] *The Sadtler Standard Spectra*, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[8] N. R. Kuloor, D. M. Newitt, and J. S. Bateman in *Thermodynamic Functions of Gases*, F. Din, editor, *1962*, Volume 2, p. 131, Butterworth, Inc., Washington, D. C.

[9] **Ibid.**, pp. 142–144.

[10] **Ibid.**, pp. 140–141.

[11] **Ibid.**, pp. 136–139.

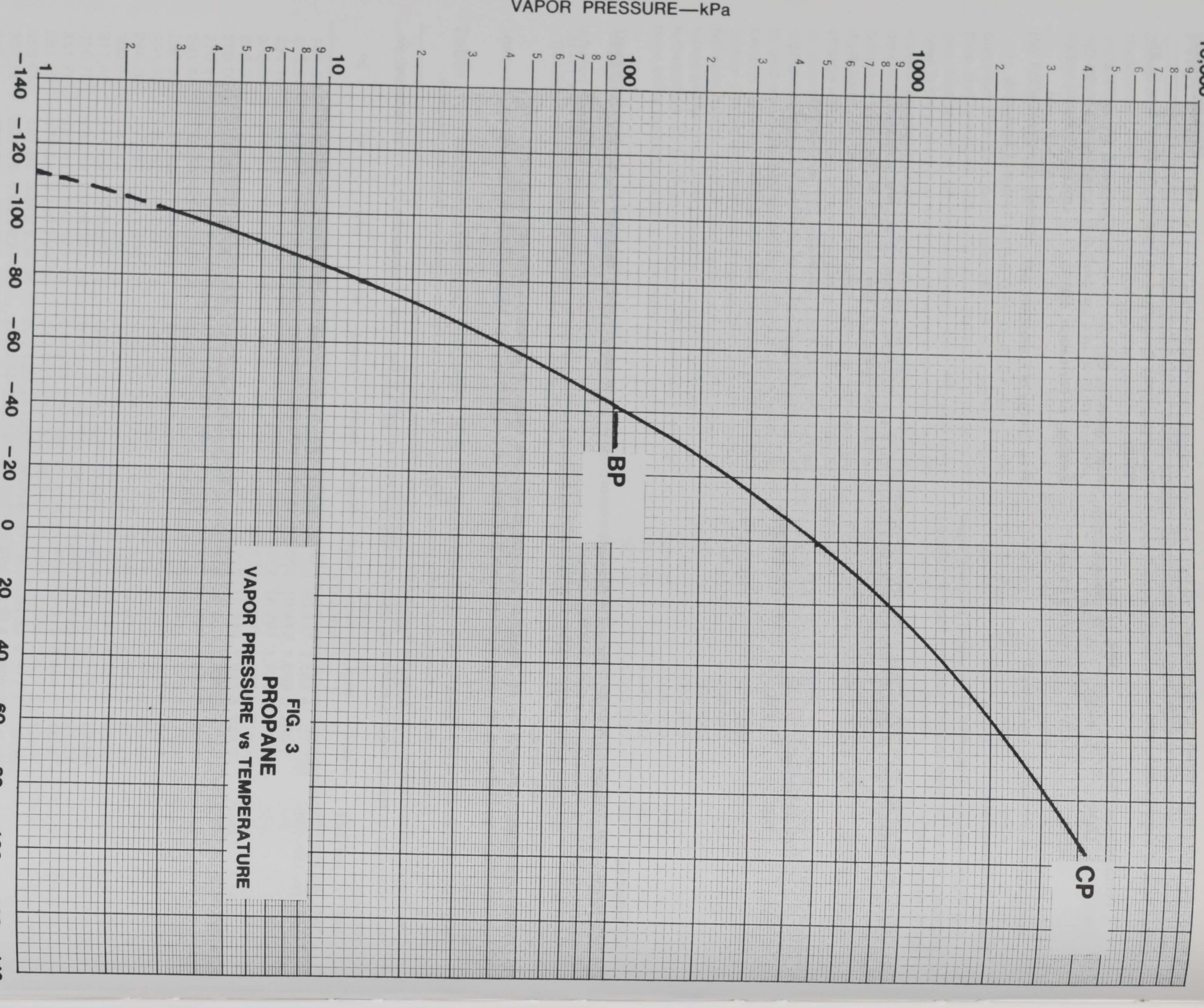


FIG. 3
PROPANE
VAPOR PRESSURE vs TEMPERATURE

Matheson®

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED PROPANE

H, ENTHALPY, kJ/mol (9); **S**, ENTROPY, J/(mol·°K) (10); **V**, SPECIFIC VOLUME, cm^3/mol (11)

Pressure kPa	atm		Temperature, °K 240	260	280	300	320	340	360	380	400	440	480	520	560	600
		H	38.074	39.316	40.645	42.063	43.560	45.140	46.813	48.565	50.400	54.322	58.570	63.132	67.945	72.983
10.132	0.1	S	273.79	278.89	283.86	288.75	293.60	298.41	303.14	307.86	312.59	321.91	331.15	340.22	349.13	357.91
		V	196 400	212 900	229 400	245 800	262 300	278 700	295 100	311 600	328 000	360 900	393 700	426 600	459 400	492 300
		H	37.982	39.249	40.591	42.013	43.518	45.107	46.779	48.531	50.371	54.301	58.549	63.115	679.32	72.970
50.662	0.5	S	260.28	265.38	275.25	275.25	280.10	284.95	289.67	294.44	299.16	308.49	317.73	326.80	335.71	344.53
		V	38 830	42 200	45 540	48 870	52 200	55 510	58 820	62 130	65 430	72 040	78 630	85 230	91 810	98 380
		H	37.869	38.505	40.524	41.954	43.468	45.065	46.737	48.498	50.337	54.272	58.524	63.090	67.911	72.954
101.325	1	S	254.22	259.40	264.46	269.39	274.24	279.10	283.86	288.63	293.35	302.68	311.92	320.99	329.90	338.72
		V	19 090	20 840	22 570	24 260	25 940	27 610	29 280	30 950	32 610	35 930	39 250	42 560	45 860	49 150
		H		38.977	40.378	41.833	43.363	44.973	46.658	48.427	50.271	54.218	58.478	63.048	67.878	72.920
202.650	2	S		253.00	258.23	263.29	268.22	273.12	277.92	282.73	287.50	296.87	306.11	315.18	324.13	332.95
		V		10 150	11 060	11 940	12 800	13 660	14 510	15 360	16 200	17 880	19 550	21 230	22 890	24 540
		H			39.830	41.419	43.033	44.697	46.411	48.205	50.066	54.046	58.332	62.923	67.769	72.824
506.625	5	S			249.20	254.72	259.86	264.92	269.85	274.70	279.51	288.96	298.20	307.32	316.31	325.13
		V			4 103	4 513	4 902	5 276	5 641	5 998	6 351	7 047	7 738	8 423	9 100	9 768
		H					42.339	44.191	45.993	47.829	49.727	53.754	58.085	62.710	67.585	72.661
1 013.250	10	S					252.75	258.15	263.29	268.31	273.20	282.77	292.10	301.26	310.25	319.15
		V					2 241	2 464	2 673	2 873	3 064	3 436	3 800	4 156	4 504	4 845
		H						42.815	45.006	46.993	48.995	53.156	57.571	62.271	67.200	72.326
2 026.500	20	S						249.24	255.51	260.95	271.11	276.04	285.66	294.98	304.06	312.96
		V						1 014	1 165	1 296	1 416	1 628	1 830	2 024	2 210	2 387
		H								44.279	49.397	51.759	56.480	61.326	66.418	71.645
4 053.000	40	S								249.49	256.60	267.93	278.22	287.96	297.24	306.19
		V								457.1	568.0	721.3	845.7	959.6	1 063	1 159
		H								37.756	43.359	50.082	55.271	60.418	65.636	70.972
6 079.500	60	S								231.39	245.69	261.74	272.99	283.19	292.77	301.88
		V								140.3	248.2	415.0	520.3	607.7	684.3	753.6
		H								36.606	40.248	48.159	53.983	59.503	64.922	70.357
8 106.000	80	S								227.37	236.70	255.64	268.27	279.30	289.30	298.66
		V								122.0	150.5	266.9	359.5	433.8	497.7	553.8
		H								36.176	39.374	46.227	52.708	58.650	64.244	69.784
10 132.500	100	S								225.49	233.73	250.04	264.13	276.04	286.45	295.99
		V								114.6	130.1	194.2	269.8	333.7	388.8	436.9
		H								35.549	38.166	43.685	49.526	55.531	61.547	67.472
20 265.000	200	S								221.02	227.75	240.92	253.63	265.63	276.71	286.96
		V								100.2	105.9	122.4	143.8	168.3	195.6	224.1
		H								35.582	38.112	43.409	49.008	54.836	60.736	66.556
25 331.250	250	S								219.89	226.41	239.00	251.16	262.83	273.74	283.78
		V								96.7	101.4	113.6	129.3	146.9	165.7	185.4
		H								35.657	38.128	43.296	48.753			
30 397.500	300	S								218.89	225.20	237.49	249.37			
		V								94.3	98.6	108.6	120.3			
		H								35.774	38.199	43.284	48.652			
35 463.750	350	S								217.92	224.15	236.24	247.95			
		V								92.3	96.1	104.6	114.2			
		H								37.104	40.775	43.326	48.640			
40 530.000	400	S								217.05	223.19	235.15	246.69			
		V								90.4	94.0	101.4	109.6			

PROPYLENE

(Synonym: Propene)
(Formula: $CH_3CH{:}CH_2$ or C_3H_6)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.042 081 kg
One Mole of C_3H_6	0.042 081 kg
Specific Volume @ 21.1 °C, 101.325 kPa	565.6 dm^3/kg; 9.06 ft^3 lb
Vapor Pressure @ 21.1 °C	1 043 kPa; 10.43 bar; 151.3 psia; 10.3 atm
Boiling Point @ 101.325 kPa	225.45 °K; −47.7 °C; −53.9 °F
Triple Point	87.90 °K; −185.2 °C; −301.4 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	1.785 5 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	1.48
Density, Liquid @ Saturation Pressure @ 20 °C	0.513 9 kg/l
Critical Temperature	364.95 °K; 91.8 °C; 197.2 °F
Critical Pressure	4 260 kPa; 42.6 bar; 670.1 psia; 45.6 atm
Critical Volume	4.301 dm^3/kg
Critical Density	0.233 kg/dm^3
Critical Compressibility Factor	0.275
Latent Heat of Fusion @ 87.90 °K	71.354 kJ/kg; 17.054 kcal/kg
Flammability Limits In Air	2.0–11.1% (by volume)
Dipole Moment, Gas	1.221×10^{-30} C.m; 0.366 D
Molar Specific Heat, Gas @ 101.325 kPa @ 15.6 °C	
@ Constant Pressure	62.345 J/(mol·°K)
@ Constant Volume	54.035 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 15.6 °C, Cp/Cv	1.154
Molar Specific Heat, Liquid @ Saturation Pressure @ −49.8 °C	91.555 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.008 45 mPa·s; 0.008 45 cP
Viscosity, Liquid @ −40 °C	0.140 mPa·s; 0.140 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.017 78 W/(m·°K); 42.5×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −40 °C	0.137 03 W/(m·°K); 327.5×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −40 °C	15.8 mN/m; 15.8 dyn/cm
Solubility In Water @ 101.325 kPa (partial pressure of C_3H_6) @ 20 °C	22.05 cm^3/100 ml water
Dielectric Constant, Liquid @ 20 °C	1.875
Autoignition Temperature	753.15 °K; 480.0 °C; 896.0 °F
Flash Point	165.15 °K; −108.0 °C; −162.4 °F
Heat of Combustion, Gas @ 25 °C and Constant Pressure	
Gross, to form H_2O(liq) + CO_2(gas)	2 058.49 kJ/mol; 11 692 kcal/kg
Net, to form H_2O(gas) + CO_2(gas)	1 926.44 kJ/mol; 10 942 kcal/kg

Description

At room temperature and atmospheric pressure, propylene is a flammable, colorless, nontoxic gas. It is one of a group of liquefied petroleum gases. It is shipped in cylinders, cargo tanks, portable tanks, single unit tank cars, and ton multiunit tank cars as a liquefied compressed gas under its own vapor pressure of 942 kPa (136.5 psig) at 21.1 °C.

Specifications

Matheson supplies two grades of propylene, the specifications of which are given below.

1. Research Purity Grade

This grade of propylene is of the highest purity that is available. A typical lot purity of the liquid phase is 99.70 mol % minimum.

Matheson

2. C.P. Grade

This grade has a minimum purity of 99 mol % in the liquid phase.

Uses

Propylene is used principally in organic synthesis to produce the following materials: acetone, isopropylbenzene, isopropyl alcohol, isopropyl halides, and propylene oxide. Propylene is also being polymerized to form polypropylene plastic.

Toxicity

Propylene is classified as a simple asphyxiant and anesthetic. This material can only be considered a mild anesthetic and high concentrations are necessary to induce a marked physiological effect which will dilute the oxygen of the air to a level which will not support life. Propylene does not have any significant toxic properties. The 1979 ACGIH has established propylene as a simple asphyxiant.

Precautions in Handling and Storage

The hazards due to the handling of propylene stem mainly from its extreme flammability. Store and use propylene cylinders in well-ventilated areas away from heat and all ignition sources such as flames and sparks. Never use flames to detect flammable gas leaks, use soap water solution. Do not use propylene around sparking motors or other nonexplosion-proof equipment. Do not store reserve stocks of propylene cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all lines and equipment used with propylene.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

All fittings and joints should be painted with soap solution to detect leaks, which will be indicated by bubble formation. Never use a flame to detect leaks.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-A.

Materials of Construction

Since propylene is a noncorrosive gas any common or commercially available metal may be used. However, piping systems or vessels to contain propylene should be designed to have a working pressure as specified by competent engineers using a safety factor conforming to the A.S.M.E. code for pressure piping.

Cylinder and Valve Description

DOT approved cylinders containing propylene are usually of the low pressure type having a rated service pressure of 1 034 kPa (150 psig) or more. Cylinders of propylene are equipped with valves having Compressed Gas Association (CGA) valve outlet No. 510 having a thread size of 0.885 inch diameter-14 threads per inch, left-hand internal threads accepting a bullet-shaped nipple. See Figure 1 for illustration of the valve outlet and mating connection. This valve outlet is standard for all liquefied petroleum gases. Valves used in this service by Matheson are of the diaphragm type and contain no packing. They are, therefore, relatively lead-free and require no packing adjustments. Lecture bottles have a special 5/16"-32 threads per inch, female outlet and a 9/16"-18 threads per inch, male dual valve outlet.

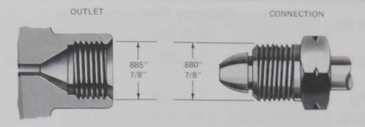


Fig. 1. CONNECTION 510 .885"-14 LH EXT. accepting a Bullet Shaped Nipple

Safety Devices

A number of different safety devices are permitted on cylinders containing propylene. A frangible disc is allowed in cylinders having a minimum required test pressure of 20 680 kPa (3 000 psig) or higher, and is required in only one end of the container. A 73.9 °C (165 °F) fusible metal may be used; however, when cylinders are over 30 inches long, exclusive of the neck, this device is required in both ends. A frangible disc backed up with 73.9 °C (165 °F) fusible metal is permitted in cylinders having a minimum required test pressure of 20 680 kPa (3 000 psig) or higher and when cylinders are over 30 inches long, exclusive of the neck, this device is required at both ends. The most commonly used safety device, which is employed by Matheson, is the spring-loaded safety relief valve. If cylinder pressure becomes dangerously high, usually due to overheating, the safety relief device with open (at approximately 2 590 kPa (375 psig)) and release propylene gas until the pressure again returns to a safe level.

Recommended Controls

Automatic Pressure Regulators

Matheson supplies single stage regulator Model 1P-510 for use with C.P. Grade propylene. This regulator has a brass body, neoprene diaphragm, and neoprene seat. It has a delivery pressure range of 28–240 kPa (4–35 psig). It is equipped with a delivery pressure gauge and needle valve for accurate flow control. No tank gauge is supplied since the vapor pressure of the gas over liquid propylene will remain constant as long as any liquid remains in the cylinder; therefore, the pressure is no indication of cylinder content. A tank gauge can be supplied, however, if requested.

For low pressure regulation Matheson supplies a Model 70 regulator constructed of a forged aluminum body and Buna N diaphragm. This regulator is constructed with an oversize, pancake body to allow sensitive and accurate low pressure control. Three pressure ranges are available as follows:

Matheson

Model No.	Delivery Pressure Range kPa	mbar (g)	psig
70B-510	0.5–3.0	5–30	2–12 inches water column
70-510	3.4–34.5	34–345	0.5–5.0 psig
70A-510	34.5–68.9	345–689	5–10 psig

This regulator is designed primarily for liquefied petroleum gases where it is particularly suited for fuel gas burner operation, since its steady low pressure delivery permits a stable flame to be obtained.

Regulator Model 3321 of brass construction, neoprene diaphragm and Kel-F seat is recommended for use with lecture bottles of C.P. Grade propylene. It has a delivery pressure range of 28–410 kPa (4–60 psig).

Single stage regulators Model 19S-510 and Model 71S-510 are recommended for use with Research Purity Grade propylene. The 19S regulator has a brass body, German silver diaphragm, nylon seat, and aluminum and nylon gaskets, and a diaphragm packless outlet valve with a ¼" Gyrolok tube fitting. It has a delivery pressure range of 0–170 kPa (0–25 psig).

The Model 71S regulator has an aluminum body, a large diaphragm of type 302 stainless steel, Teflon seat, and type 303 stainless steel needle valve outlet with ¼" NPT male and hose connection. It has a delivery pressure range of 3.4–40 kPa (0.5–6 psig).

Manual Controls

Matheson needle valve Model 50–510, for use with C.P. Grade, is a brass bar stock valve that is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a hose connection, ¼" tube fitting, or ¼" NPT male or female pipe. It should be used only where manual flow control is needed and should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. A Model 31B manual needle valve can be supplied for use with lecture bottles, where accurate flow control is desired.

Manual control Model No. 4351-510 of diaphragm packless construction and ¼" Gyrolok outlet connection is recommended for use with Research Purity Grade propylene.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 15 mm tubes and floats or Matheson Series 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Propylene is classified by the DOT as a flammable, compressed gas and is shipped with the required "Red Gas Label".

Commercial Preparation

Propylene is obtained from petroleum oils during the refining of gasoline and to a lesser extent by splitting, cracking, and reforming hydrocarbon mixtures.

Chemical Properties

Propylene is a member of the alkene or olefin series of hydrocarbons. The alkanes being unsaturated will undergo a wide variety of addition reactions. Some of the general reactions of alkenes are as follows:

(a) The alkenes combine with hydrogen halides forming alkyl halides, the descending order of reactivity of the former being HI, HBr, HCl. Normal addition follows Markownikoff's rule, the halogen atom becoming attached to the carbon carrying the fewest hydrogen atoms. Peroxides reverse the direction of addition of hydrogen halides to alkenes.

(b) The alkenes combine with halogens; the order of decreasing addition rate being chlorine, bromine, iodine. At higher temperatures, substitution on the carbon adjacent to the doubly bonded carbon atoms can occur.

(c) The alkenes are hydrogenated to the corresponding alkanes in the presence of suitable catalysts (platinum, palladium, Raney nickel).

(d) The alkenes combine with concentrated sulfuric acid forming alkyl hydrogen sulfates which on hydrolysis yield alcohols. The method is a convenient one for the hydration of double bonds.

(e) With positive halogen compounds, like N-bromosuccinimide, the alkenes are halogenated at the alpha carbon—allylic halogenation.

(f) With hypochlorous acid, the alkenes give chlorohydrins.

(g) In the presence of aluminum chloride, the alkenes combine with acyl halides giving halogeno ketones.

(h) The alkenes combine with carbon monoxide and hydrogen in the presence of cobalt under high pressure to form aldehydes.

(i) The alkenes are readily oxidized by a variety of oxidizing agents, e.g., potassium permanganate, hydrogen peroxide, perbenzoic acid, etc.

(j) The alkenes can be polymerized to polyalkenes under suitable conditions, the polymerization being catalyzed by aluminum chloride or boron trifluoride.

(k) At elevated temperatures and pressures, and in the presence of sulfuric acid or other catalysts, alkanes may add to alkenes.

(l) The alkenes may be isomerized by heating alone or in the presence of catalysts.

Thermodynamic and Detailed Physical Data

Molecular Structure

Propylene has C_s point group symmetry and a symmetry number of three. In propylene the C═C bond is nonsymmetrical in comparison to the C═C bond in ethylene which is symmetrical. A slight distortion for the C═C bond is produced and the C—C bond distance itself is shortened to 1.51 Å (1.51×10^{-10} m) relative to 1.54 Å (1.54×10^{-10} m) in ethane. Three resonance structures are considered as contributing to the stabilization of propylene (2):

$$CH_3{-}CH{=}CH_2 \leftrightarrow CH_2{=}\overset{H+}{\underset{|}{C}}H{-}\overset{-}{\underset{|}{C}}H_2 \leftrightarrow CH_2{=}\underset{|}{\overset{H}{C}}{-}CH_2$$

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous propylene.

Vapor Pressure (3)

Vapor pressures up to 101.325 kPa (760 mmHg) are shown below.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
141.25	0.133	1.33	1
152.45	0.667	6.67	5
161.05	1.333	13.3	10
168.45	2.666	26.7	20
176.65	5.333	53.3	40
181.85	7.999	80.0	60
189.05	13.332	133	100
199.85	26.664	267	200
212.25	53.329	533	400
225.45	101.325	1 013.25	760

Vapor pressures above 1 atm are shown below.

Temperature, °K	Vapor Pressure kPa	bar	atm
225.45	101.325	1.013 25	1
241.75	202.65	2.03	2
268.35	506.625	5.07	5
292.95	1 013.250	10.1	10
322.65	2 026.500	20.3	20
343.15	3 039.750	30.4	30
358.15	4 053.000	40.5	40

For additional vapor pressure data, see Table 1 and Figure 3.

Latent Heat of Vaporization, ΔHv @ 225.45 °K	18.418 kJ/mol 4.402 kcal/mol

For additional ΔHv values, see Table 1.

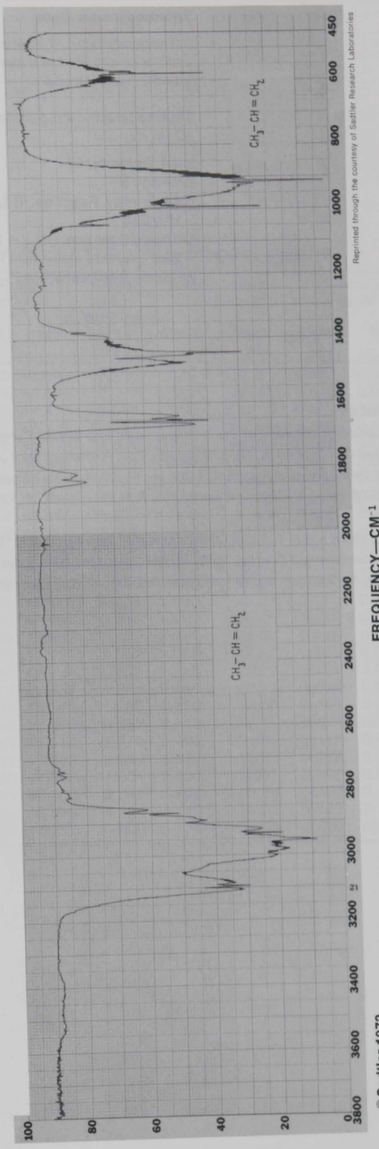


Fig. 2. Infrared spectrum of gaseous propylene; 10-cm path length cell, with KBr optics; cell pressure (complete scan): 7 999 kPa (60 mmHg) (5).

Thermodynamic Data

Thermodynamic properties for saturated propylene liquid and vapor and for the superheated vapor are shown in Tables 1 and 2, respectively.

Thermodynamic Properties of Propylene As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	63.890 J/(mol·°K)
Entropy, S°	266.939 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_0^\circ)/298$	−221.543 J/(mol·°K)
Enthalpy Function, $(H_{298}^\circ - H_0^\circ)/298$	45.355 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	13.544 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of propylene, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] M. J. S. Dewar, *Hyperconjugation, 1962*, pp. 50, 62–64, The Ronald Press Co., New York, New York.

[3] *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p. 3–59, 3–62, McGraw-Hill Book Co., Inc., New York, New York.

[4] J. E. Kilpatrick and K. S. Pitzer, *J. Research Natl. Bur. Stand.* 37, 163–171 (1946).

[5] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[6] L. Canjar, M. Goldman, and H. Marchman, *Ind. Eng. Chem.* 43, 1186 (1951).

Table 1. THERMODYNAMIC PROPERTY OF SATURATED PROPYLENE (6)

Temperature		Pressure		Entropy J/(mol·°K)		Enthalpy kJ/mol		Latent Heat of Vaporization kJ/mol	Specific Volume dm^3/kg		Density kg/m^3	
°K	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
225.45	−53.86	101.325	1.000	168.021	249.663	26.000	44.408	18.408	1.629 4	422.9	0.613 7	0.002 36
227.59	−50.0	111.660	1.102	168.866	249.311	26.234	44.545	18.311	1.640	386.7	0.610	0.002 59
233.15	−40.0	141.956	1.401	171.190	248.606	26.750	44.803	18.053	1.660	308.1	0.602	0.003 25
238.71	−30.0	178.433	1.761	173.408	247.902	27.257	45.043	17.786	1.680	250.6	0.595	0.003 99
244.26	−20.0	221.598	2.187	175.697	247.374	27.769	45.278	17.509	1.700	205.0	0.588	0.004 88
249.82	−10.0	272.159	2.686	177.757	246.670	28.276	45.497	17.221	1.730	169.4	0.578	0.005 90
255.37	0.0	330.623	3.263	179.905	246.142	28.806	45.726	16.920	1.750	140.8	0.571	0.007 10
260.93	10.0	398.410	3.932	181.983	245.613	29.345	45.950	16.605	1.770	117.7	0.565	0.008 50
266.48	20.0	505.004	4.984	184.025	245.085	29.888	46.163	16.275	1.800	99.01	0.556	0.010 10
272.04	30.0	564.887	5.575	186.015	244.557	30.438	46.366	15.928	1.820	83.84	0.549	0.011 93
277.59	40.0	665.503	6.568	187.969	244.029	30.992	46.653	15.661	1.850	71.29	0.541	0.014 03
283.15	50.0	778.683	7.685	189.906	243.501	31.576	46.850	15.274	1.880	60.93	0.532	0.016 41
288.71	60.0	905.744	8.939	191.925	242.972	32.128	46.896	14.768	1.920	52.31	0.521	0.019 12
294.26	70.0	1 047.295	10.336	193.726	242.444	32.709	47.143	14.434	1.950	45.07	0.513	0.022 19
299.82	80.0	1 204.552	11.888	195.804	242.092	33.286	47.167	13.881	1.980	38.96	0.505	0.025 67
305.37	90.0	1 377.919	13.599	197.688	241.564	33.889	47.292	13.403	2.020	33.90	0.495	0.029 50
310.93	100.0	1 569.119	15.486	199.625	241.036	34.495	47.397	12.902	2.060	29.47	0.485	0.033 93
316.48	110.0	1 778.456	17.552	201.491	240.683	35.097	47.474	12.377	2.110	25.72	0.474	0.038 88
322.04	120.0	2 007.654	19.814	203.357	240.155	35.713	47.537	11.824	2.160	22.47	0.463	0.044 50
327.59	130.0	2 258.129	22.286	205.118	239.451	36.308	47.576	11.268	2.230	19.60	0.448	0.051 02
333.15	140.0	2 530.896	24.978	207.002	238.923	36.962	47.599	10.637	2.310	17.11	0.433	0.058 44
338.71	150.0	2 828.386	27.914	209.097	238.219	37.665	47.544	9.879	2.400	14.80	0.417	0.067 57
344.26	160.0	3 150.701	31.095	211.421	237.338	38.495	47.444	8.949	2.510	12.67	0.398	0.078 93
349.82	170.0	3 500.475	34.547	214.045	236.282	39.490	47.291	7.801	2.620	10.61	0.382	0.094 25
355.37	180.0	3 880.038	38.293	217.073	235.049	40.615	47.003	6.388	2.790	8.62	0.358	0.116 01
360.93	190.0	4 294.660	42.385	221.756	233.641	42.074	46.338	4.264	3.110	6.62	0.322	0.151 06
364.91	197.17	4 621.332	45.609	228.218	228.218	44.785	44.785	0.000	4.539	4.539	0.220	0.220 03

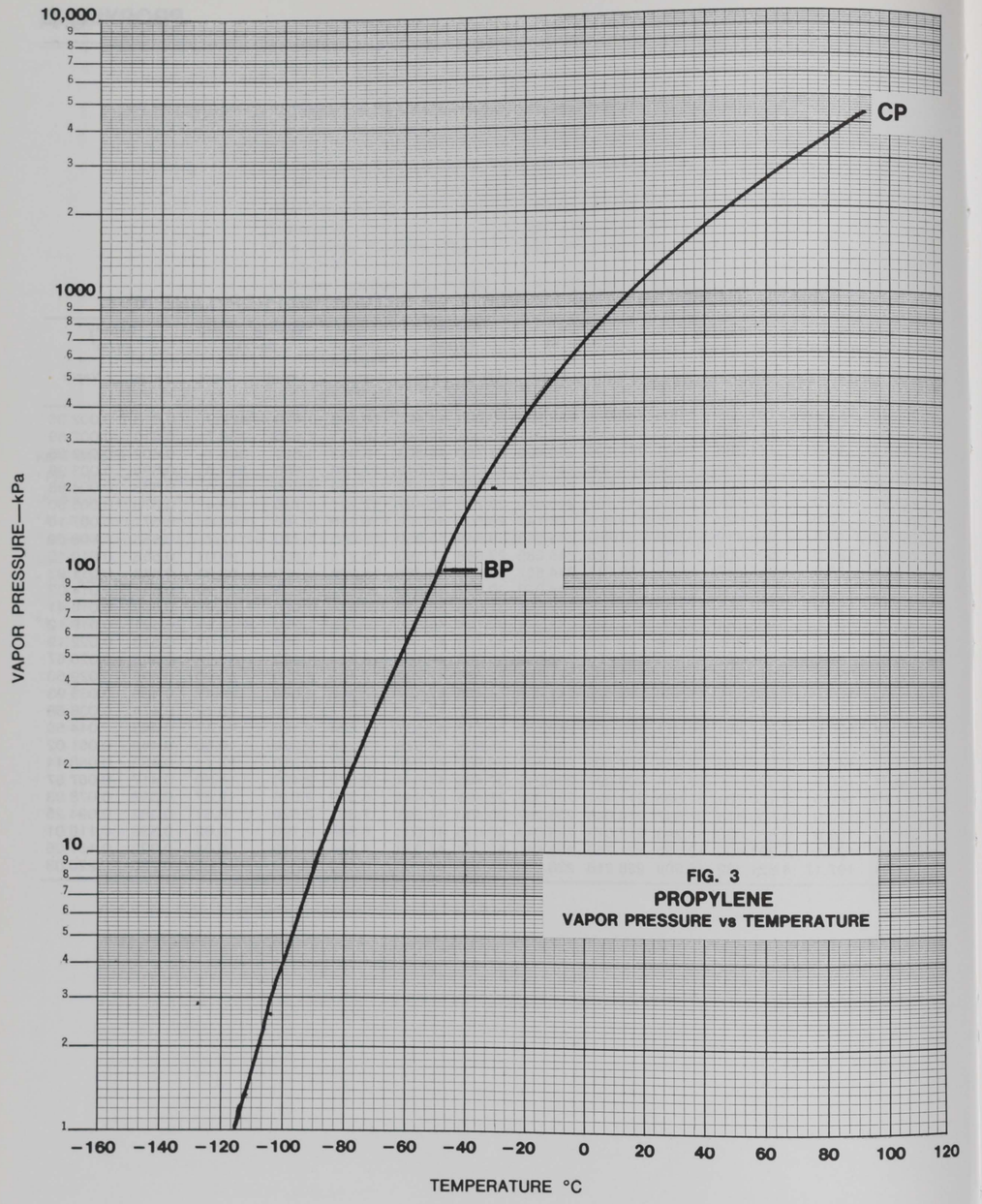


FIG. 3
PROPYLENE
VAPOR PRESSURE vs TEMPERATURE

Matheson

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED PROPYLENE (6)

H, ENTHALPY, kJ/mol; **S**, ENTROPY, J/(mol·°K); **V**, SPECIFIC VOLUME, dm^3/kg

Pressure kPa	atm		Temperature, °K 233.15	255.37	277.59	299.82	322.04	344.26	366.48	394.26	422.04	477.59
101.325	1	H	44.887 3	46.158 9	47.508 7	48.907 5	50.423 6	51.998 4	53.631 9	55.774 1	58.033 6	62.875 4
		S	251.600	257.058	262.164	266.037	271.143	276.073	280.827	286.637	292.271	303.187
		V	439.7	485.5	531.1	576.6	622.0	666.7	711.3	766.4	821.2	930.6
202.650	2	H		45.973 0	47.058 8	48.780 3	50.306 2	51.900 6	53.553 7	55.705 6	57.965 1	62.836 3
		S		250.719	256.001	260.931	265.861	270.615	275.369	281.003	286.637	297.377
		V		233.7	258.5	283.1	306.5	329.1	351.5	379.6	407.7	462.7
405.300	4	H			47.019 6	48.496 6	50.081 2	51.705 0	53.387 4	55.568 7	57.857 5	62.738 5
		S			249.487	254.593	259.699	264.452	269.206	275.017	280.651	291.567
		V			124.5	137.0	149.8	161.9	173.4	187.7	201.8	230.0
607.950	6	H			46.667 5	48.203 2	49.826 9	51.509 3	53.221 1	55.431 7	57.740 2	62.650 5
		S			244.909	250.367	255.649	260.755	265.509	271.319	276.953	288.045
		V			78.91	88.15	96.89	105.5	113.6	123.3	133.0	152.2
810.600	8	H				47.880 4	49.572 6	51.284 4	53.035 3	55.294 8	57.632 6	62.572 2
		S				247.374	252.656	257.938	262.692	268.678	274.488	285.561
		V				63.68	70.61	77.41	83.65	91.21	98.76	113.6
1 013.250	10	H				47.538 1	49.308 5	51.069 2	52.849 4	55.148 1	57.515 2	62.484 2
		S				244.557	250.191	255.473	260.403	266.565	272.376	283.468
		V				48.88	54.94	60.37	65.42	71.98	78.10	90.21
1 519.875	15	H					48.516 2	50.443 2	52.360 3	54.766 6	57.212 0	62.278 8
		S					244.909	250.719	256.177	262.516	268.502	279.770
		V					33.52	37.89	41.83	46.45	50.82	59.24
2 026.50	20	H						49.768 2	51.812 6	54.365 5	56.889 2	62.053 8
		S						246.846	252.656	259.347	265.509	277.129
		V						26.41	29.65	33.46	37.02	43.70
3 039.75	30	H							50.541 0	55.255 7	56.214 2	61.613 6
		S							246.318	254.241	261.107	273.080
		V							17.23	20.48	23.29	28.16
4 053.00	40	H							48.672 7	52.467 9	55.480 6	61.134 3
		S							239.979	249.839	257.234	269.911
		V							10.18	13.80	16.29	20.35
5 066.25	50	H								51.206 1	54.659 0	60.635 5
		S								245.261	253.888	267.270
		V								9.49	12.05	15.67
6 079.50	60	H								49.523 7	53.739 5	60.117 1
		S								240.331	250.719	264.981
		V								6.49	9.18	12.61
7 092.75	70	H								47.459 8	52.722 2	59.598 6
		S								234.697	247.550	262.868
		V								4.43	7.18	10.43

Matheson

SILANE

(Synonyms: Monosilane; Silicon Tetrahydride)
(Formula: SiH_4)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.032 118 kg
One Mole of SiH_4	0.032 118 kg
Specific Volume @ 21.1°C, 101.325 kPa	751.8 dm^3/kg; 12.04 ft^3/lb
Boiling Point @ 101.325 kPa	161.65 °K; −111.5 °C; −168.7 °F
Melting Point	88.15 °K; −185.0 °C; −301.0 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	1.342 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	1.114
Density, Liquid @ 88.15 °K	0.711 kg/l
Critical Temperature	269.70 °K; −3.4 °C; 25.8 °F
Critical Pressure	4 843 kPa; 48.43 bar; 702.5 psia; 47.8 atm
Critical Volume	4.132 dm^3/kg
Critical Density	0.242 kg/dm^3
Critical Compressibility Factor	0.287
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.010 92 mPa·s; 0.010 92 cP
Trouton Constant	72.383 J/(mol·°K); 17.3 cal/(mol·°K)
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	42.844 J/(mol·°K)

Description

Silane is a colorless gas with a repulsive odor at room temperature and atmospheric pressure. It is stable indefinitely in metal containers. Silane in the pure state is spontaneously flammable in air. It is shipped in various size steel cylinders as a nonliquefied gas at various pressures, the highest cylinder pressure being 8625 kPa (1250 psig) at 21.1 °C.

Specifications

Silane supplied by Matheson is a Semiconductor Grade material with a minimum purity of 99.99 mole %. Deposits formed from silane will be of the N-type with a minimum resistivity of 100 ohm-cm.

Uses

Silane of Semiconductor Grade offers a source of high purity silicon for epitaxial and thin film deposits, and for the formation of high purity silicon oxides.

Effects In Man and Toxicity (2)

Little is known of the toxicity of silane except that breathing this gas may cause headache and nausea. The hydrolysis of silane in the body tissues would form silicic acid or hydrated silica. The offensive odors of most of these gases should be taken as a warning of the presence of dangerous concentrations of the gases.

The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 0.5 ppm (0.7 mg/m^3) for silane.

First Aid Treatment (2)

Remove the victim promptly to an uncontaminated atmosphere. Keep the victim warm (not hot) and quiet. Administer pure oxygen. If breathing is weak and has stopped, give artificial respiration with simultaneous administration of oxygen.

Suggestions for Medical Treaament

Use intermittent positive pressure oxygen for pulmonary edema. If muscle spasm or muscle tremor is present, use barbiturates to prevent convulsions. Treat anemia, if severe, by transfusion. Treatment otherwise is symptomatic and supportive.

Precautions in Handling and Storage

The following specific precautions should be observed in handling silane:

1. Store at positive pressures.
2. Piping and equipment should be thoroughly pressure-checked above working pressure and be genuinely leak-tight.
3. Do not condense silane (−110 °C or less). Serious accidents have occurred with liquid and solid silane.
4. Evacuate piping and systems and purge with inert gas (nitrogen, helium, etc.) before introducing silane.

5. Vent with carrier gas to outdoors—no hoods—through pipe small enough to insure no back diffusion. Stainless steel or iron pipe is preferred.
6. Use diaphragm pack-less valves with resilient seats such as Teflon.
7. Remove back plates on rotameters and pressure gauge covers.
8. Pressure regulators used with silane should have metal diaphragms to allow complete evacuation.
9. Be very cautious about using silane in systems with halogenated compounds. Even a trace of free halogen can be violently explosive with silane.
10. Mixtures down to 1.0% silane in hydrogen and/or nitrogen have been found to be spontaneously flammable when mixed with air. At very high escape velocities mixtures as high as 10% may not spontaneously ignite. Venting of hydrogen-silane mixtures of any concentration should be done as far for pure silane. Preferably, they should be burned.
11. Ground all lines and equipment used with silane.
12. Do not store reserve stocks of silane with cylinders containing oxygen or other highly oxidizing or flammable materials.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Piping and equipment should be thoroughly pressure-checked with an inert gas and soapy water above working pressures and be completely leak-tight. Leaks in a system containing silane will be indicated by flames. Do not attempt to extinguish but shut off source of silane immediately.

Materials of Construction

Piping and accessories leading to equipment for the thermal decomposition of silane may be of iron or steel construction and should be adequately designed to withstand pressures to be encountered.

Cylinder and Valve Description

Silane is shipped in 4 different size DOT approved cylinders, namely, 1Y, 1A, 1X, and 3. 1X and 3 cylinders are equipped with Compressed Gas Association (CGA) 510 valve outlet connections, which is a 0.885 inch left-hand internal thread

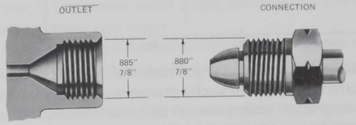


Fig. 1. CONNECTION 510 .885"-14 LH INT. accepting a Bullet Shaped Nipple

accepting a bullet-shaped nipple (see Figure 1 for an illustration).

1Y and 1A cylinders are equipped with CGA 350 valve outlet connections, which is a 0.825 inch left-hand external thread accepting a round-shaped nipple.

Safety Devices

Cylinders containing silane are not equipped with safety devices, and therefore should be stored away from sources of heat to avoid the development of dangerous pressures within the cylinder.

Recommended Controls

Automatic Pressure Regulators

Single stage regulators, Models 19S-510 and 3501-510 are recommended for use with size 1X and 3 cylinders only. These metal diaphragm high purity regulators have a delivery pressure range of 0–170 kPa (0–25 psig).

Single stage metal diaphragm regulators Models 3502-350 and 19SM-350 are recommended for use with 1Y and 1A cylinders only. These regulators have delivery pressure ranges of 0–170 kPa (0–25 psig). Two stage regulators Models 3800-350 and 3104-350, having delivery pressure ranges of 28–620 kPa (4–90 psig) and 28–690 kPa (4–100 psig), respectively, are recommended for use with 1Y and 1A cylinders only.

Flowmeters

Matheson Series 7600 laboratory brass or stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass or stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Silane is classified by the DOT as a flammable gas and is shipped under the required "Red Gas Label".

Chemical Preparation

Treatment of magnesium silicide Mg_2Si with 20% HCl gives mainly hydrogen along with a mixture of silicon hydrides, which can be separated by fractional distillation. Silane can be prepared in 70–80% yields by reaction of Mg_2Si with ammonium bromide in liquid ammonia in a current of hydrogen. Reduction of silicon tetrachloride with lithium, magnesium, sodium or calcium aluminum hydride in ethyl ether or tetrahydrofuran gives silane in high yields.

Chemical Properties

Silane is stable to neutral or acid water, but in the presence of base, even the traces provided by glass vessels, it is rapidly

hydrolyzed to hydrated silica. Silane is a strong reducing agent. Halogenation reactions with chlorine or bromine are explosively violent at room temperature. Decomposition of silane into silicon and hydrogen begins at about 400 °C and proceeds rapidly at temperatures above 600 °C. For additional reactions of silane and other silicon hydrides see Reference 3.

Thermodynamic and Detailed Physical Data

Molecular Structure

Silane is a tetrahedral molecule, with T_d point group symmetry and a symmetry number of twelve, with the following structural parameters: bond distance: Si-H 1.457 [Å] (1.457 × 10^{-10} m); bond angle: H-Si-H 109.47°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of a typical sample of silane isolated in an argon matrix at 14 °K.

Vapor Pressure (5)

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
93.85	0.133	1.33	1
104.55	0.667	6.67	5
110.15	1.333	13.3	10
116.25	2.666	26.7	20
122.85	5.333	53.3	40
126.85	7.999	80.0	60
132.65	13.332	133	100
141.55	26.664	267	200
151.15	53.329	533	400
161.65	101.325	1 013.25	760

Latent Heat of Vaporization

@ 161.65 °K: 12.385 kJ/mol; 2.96 [kcal/mol]

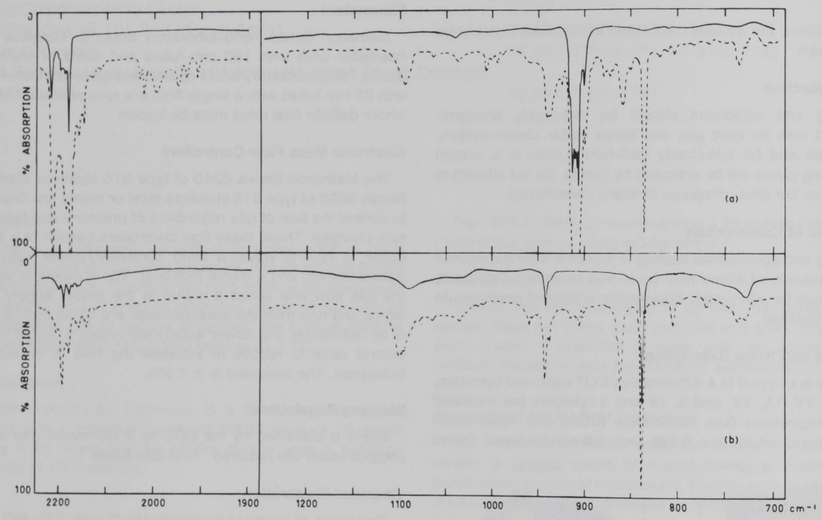


Fig. 2. (a) The infrared spectrum of a typical unphotolyzed sample of silane isolated in an argon matrix at 14 °K is shown in the solid trace of Figure 1 (a). When additional sample is added with concurrent vacuum-ultraviolet photolysis, a spectrum such as that shown by the dotted trace of Figure 2 (a) results. Prominent photolysis product absorptions at 837 and 942 cm^{-1} are readily assigned to Si_2H_6, the argon-matrix spectrum of which is shown in the solid trace of Figure 2 (b) (7).

Thermodynamic Data

Compressibility factors for silane at 21.1 °C are shown in Table 1.

Thermodynamic Properties of Silane As Ideal Gas @ 25 °C (6)

Heat Capacity, C_p°	42.827 J/(mol·°K)
Entropy, S°	204.133 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−204.133 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	10.539 kJ/mol
Enthalpy of Formation, ΔH_f°	32.635 kJ/mol
Free Energy of Formation, ΔF_f°	55.162 kJ/mol

Table 1. COMPRESSIBILITY FACTORS FOR SILANE AT 21.1 °C

Compressibility Factor	Pressure kPa	bar	atm
0.99	101.325	1.013 25	1
0.99	203	2.03	2
0.98	304	3.04	3
0.98	405	4.05	4
0.975	507	5.07	5
0.945	1 010	10.1	10
0.925	1 520	15.2	15
0.895	2 030	20.3	20
0.83	3 040	30.4	30
0.77	4 050	40.5	40
0.70	4 840	48.4	47.8

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of silane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, *2nd edition*, *1977*, pp. 60–75, Matheson, Lyndhurst, New Jersey.

[3] F. G. A. Stone, *Hydrogen Compounds of the Group IV Elements*, *1962*, pp. 11–61, Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

[4] K. Nakamoto, *Infrared Spectrum of Inorganic and Coordination Compounds*, 2nd edition, *1970*, p. 108, John Wiley & Sons, Inc., New York, New York.

[5] *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p. 3–48, McGraw-Hill Book Co., Inc., New York, New York.

[6] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[7] D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* 52, 2594 (1969).

SILICON TETRAFLUORIDE

(Synonym: Tetrafluorosilane)
(Formula: SiF_4)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.104 08 kg
One Mole of SiF_4	0.104 08 kg
Specific Volume @ 21.1 °C, 101.325 kPa	231.0 dm^3/kg; 3.7 ft^3/lb
Boiling Point @ 241 kPa	208.15 °K; −65.0 °C; −85.0 °F
Sublimation Point	178.35 °K; −94.8 °C; −138.6 °F
Melting Point	177.45 °K; −95.7 °C; −140.3 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	4.370 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	3.63
Critical Temperature	259.00 °K; −14.2 °C; 6.5 °F
Critical Pressure	3 715 kPa; 37.15 bar; 538.8 psia; 36.66 atm
Latent Heat of Sublimation @ 178.35 °K	25.648 kJ/mol; 6.130 kcal/mol
Latent Heat of Fusion @ 177.45 °K	9.510 kJ/mol; 2.273 kcal/mol

Description

At room temperature and atmospheric pressure, silicon tetrafluoride is a colorless, nonflammable, toxic gas with a suffocating odor. It is shipped as a nonliquefied gas. Cylinder pressure is 6 895 kPa (1 000 psig) at 21.1 °C.

Specifications

Silicon tetrafluoride has a minimum purity of 99.99 mole %.

Uses

Silicon tetrafluoride is chiefly in the manufacture of fluosilicic acid and its salts. Fluosilicic acid or its sodium salt is used in water fluoridation. Fluosilicic acid is also used to produce cryolite and aluminum fluoride.

Effects in Man and Toxicity (2)

The concentration that produces acute effects varies with the time of exposure; 50 ppm may be fatal if inhaled for 30–60 minutes. Less severe exposures cause irritation of the nose and eyes, smarting of the skin, some degree of conjunctival and respiratory irritation. More severe exposures can lead to severe irritation of the eyes and eyelids and to inflammation and congestion of the lungs and circulatory (cardiovascular) collapse. Skin contact with the liquid or vapor of any member of this group can cause severe burns.

Silicon tetrafluoride is readily detectable in air by its sharp, irritating odor.

No Threshold Limit Value (TLV) has as yet been established for silicon tetrafluoride.

First Aid Treatment (2)

Speed in removing the patient from the contaminated atmosphere or removing the vapor or liquid from the skin or eyes is essential. First aid must be started immediately in all cases of contact with the particular gas in any form. All affected persons should be referred to a physician, no matter how slight the injury, and the physician given a detailed account of the accident.

Inhalation

In minor exposures, remove the victim to an uncontaminated atmosphere and administer as quickly as possible 100% oxygen. It has been found helpful to expose even borderline cases to 100% oxygen at half hour intervals for 3–4 hours.

In severe exposures, the worker must be carried at once into an uncontaminated atmosphere. A physician should be called immediately and the administration of 100% oxygen should be started at once. The victim should receive oxygen under positive pressure (<4 cm) for half hour periods for at least 6 hours until breathing is easy and the color of the skin and mucous membranes is normal. He should be kept comfortably warm, but not hot. Under no circumstances should the patient be permitted to return home or to work following a severe exposure until examined and discharged by a physician who is aware of the nature of the exposure. Mild analgesics and sedatives, such as aspirin or sodium bromide, may be given if thought to be desirable by the physician, but medication is usually unnecessary when adequate oxygen has been administered immediately after exposure. Morphine and barbiturates should never be given because of their depressant effect on respiration. Cardiac and respiratory stimulants are not recommended.

Artificial respiration should not be given unless breathing has ceased.

Contact with Eyes

If the eyes have been contacted by silicon tetrafluoride, they should be flushed with water for 15 minutes. This may have to

be repeated several times. Ice compresses should be applied when not irritating. Pain can be relieved by 2 or 3 drops of 0.5% tetracaine (pontocaine). An ophthalmologist should be consulted for more definite treatment.

Contact with Skin

Workers who have had skin contact with silicon tetrafluoride should be subjected to a drenching shower of water. The clothing should be removed as rapidly as possible, even while the victim is in the shower, and medical assistance obtained immediately. It is essential that the affected area be washed with copious quantities of water for a sufficient period of time to remove all acid from the skin. The affected part should then be immersed in an ice-cold saturated solution of magnesium sulfate (Epsom salt), iced 70% alcohol, or an iced aqueous or alcoholic solution of Hyamine, a high molecular weight quaternary ammonium compound. The immersed part should be removed for 2–3 minutes every 10 minutes to relieve the discomfort. If the burn is in such an area that it is impractical to immerse the part, then iced alcohol, iced magnesium sulfate solution, or Hyamine solution should be applied in the form of saturated compresses, which should be changed at least every 2 minutes. This treatment should be continued for 1–4 hours depending on the extent of the burn. The area should then be covered with a generous quantity of paste freshly prepared from powdered U.S.P. magnesium oxide and U.S.P. glycerin. This paste should be applied daily for several days.

Precautions in Handling and Storage

(a) Workers who handle silicon tetrafluoride should wear protective clothing such as rubber or plastic aprons, rubber gloves, and suitable gas-tight chemical safety goggles. Woolen outside clothing or other acid resistant fabrics are recommended for workers handling silicon tetrafluoride.

(b) Instant-acting showers should be available in the event of an emergency.

(c) Special eye-washing fountains or similar equipment should be available for eye irrigation.

(d) Proper respiratory equipment must be provided and personnel wearing such equipment must be carefully instructed in its operation and limitations.

(e) Precautions should always be taken to prevent suckback of foreign materials into the cylinder by using a check valve, vacuum break, or trap, since a suckback may cause the development of dangerous pressures within the cylinder. The cylinder valve should be closed after each use.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Large leaks of silicon tetrafluoride will be evident by the formation of dense white fumes on contact with the atmosphere. Small leaks of silicon tetrafluoride may be detected by holding an open bottle of concentrated ammonium hydroxide solution near the site of the suspected leak (formation of dense white fumes). Wet blue litmus paper will turn pink when exposed to a silicon tetrafluoride leak.

Cylinder valve leaks can usually be corrected by tightening the valve packing nut (turn clockwise as viewed from above).

Disposal of Leaking Cylinders

Leaking cylinders of silicon tetrafluoride that cannot be corrected should be disposed of by the procedure described in Appendix II-D.

Materials of Construction

Most common metals of construction are satisfactory for handling the dry gas. Plastics suitable for certain applications are Teflon, Kel-F, Saran, polyethylene, polyvinyl chloride, and neoprene. Under moist conditions, silicon tetrafluoride is rapidly hydrolyzed and leads to corrosive conditions.

Cylinder and Valve Description

Silicon tetrafluoride is shipped in DOT approved, high pressure steel cylinders. Cylinders of silicon tetrafluoride are equipped with steel or aluminum-iron-bronze valves. The assigned standard valve outlet connection used by Matheson is Compressed Gas Association (CGA) connection No. 330. The valve outlet has a thread size of 0.825 inch with left-hand

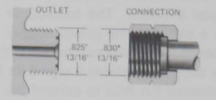


Fig. 1 CONNECTION 330 .825"-14 LH EXT. used with Flat Seat and Washer

external threads, with flat seat using a washer to seal (see Figure 1 for an illustration of the valve outlet and its mating connection). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet.

Safety Devices

Cylinders of silicon tetrafluoride contain safety devices which consist of frangible discs backed up with fusible metal, melting about 73.9 °C (165 °F). Cylinders should be stored away from sources of heat to prevent dangerous pressures from developing within the cylinder.

Recommended Controls

Automatic Pressure Regulator

Regulators Model B15B-330 and B16B-330, having delivery pressure ranges of 28–345 kPa (4-50 psig) and 345–4 480 kPa (50-650 psig), respectively, are recommended for use with silicon tetrafluoride. These regulators have chemically-deposited pure nickel on brass bodies, chemically-deposited pure nickel on nickel-silver alloy diaphragms, internal parts of monel, Kel-F seats, and monel needle valve outlets. To prevent suckback of foreign materials, a monel check valve is recommended for use with the regulators.

Manual Controls

Manual needle valve Model 55A-330, of monel bar stock, with ¼" tube fitting outlet connection is available for direct attachment to the cylinder valve outlet. It should not be used

as a pressure control since it will not prevent pressure from building up if the system becomes clogged or if the system itself is closed. Needle valve Model 60L is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory monel flowmeter units with 150 mm tubes and floats are recommended for use where definite flow rates must be known.

Monel electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8260 of monel is designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Silicon tetrafluoride is classified by the DOT as a nonflammable compressed gas and is shipped with the required "Green Label".

Commercial Preparation

Silicon tetrafluoride is obtained by treating a mixture of a fluoride and silica with sulfuric acid or by heating barium fluosilicate or by treating a mixture of sodium fluosilicate and sand with sulfuric acid.

Chemical Properties

Silicon tetrafluoride is stable and inert to oxidation and reduction. It is hydrolyzed by water according to the reaction:

$$3SiF_4 + (x + 2)H_2O \rightarrow SiO_2 \cdot xH_2O + 2H_2SiF_6.$$

It reacts with alcohols to form alkyl orthosilicates and alcoholated fluosilicic acids. Silicon tetrafluoride with trimethylamine forms the unstable solid addition compound $(CH_3)_3N \cdot SiF_4$, from which silicon tetrafluoride may be displaced by any suitable acidic substance. Silicon tetrafluoride reacts with silicon tetrachloride at 600 °C to give $SiClF_3$, $SiCl_2F_2$, and $SiCl_3F$. Silicon tetrafluoride reacts with aluminum chloride at elevated temperatures to give $SiCl_4$, but the reaction at lower temperatures (180–190 °C) yields a mixture of silicon chlorofluorides. Silicon tetrafluoride reacts with alkali metal fluorides to give fluosilicates; e.g.:

$$SiF_4 + 2NaF \rightarrow Na_2SiF_6.$$

Silicon tetrafluoride reacts with alkyl or aryl Grignard reagents according to the reaction:

$$SiF_4 + 3RMgX \rightarrow R_3SiF + 3MgFX.$$

Thermodynamic and Detailed Physical Data

Molecular Structure

Silicon tetrafluoride is a tetrahedral molecule with T_d point group symmetry and a symmetry number of twelve, with the following structural parameters: bond distance: Si-F 1.54 Å (1.54×10^{-10} m); bond angle: F-Si-F 109.47°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous silicon tetrafluoride.

Sublimation Pressure (3)

The sublimation pressure is shown below.

Temperature, °K	Sublimation Pressure		
	kPa	mbar	mmHg
129.15	0.133	1.33	1
138.35	0.667	6.67	5
142.75	1.333	13.3	10
147.25	2.666	26.7	20
152.35	5.333	53.3	40
155.65	7.999	80.0	60
159.85	13.332	133	100
165.95	26.664	267	200
172.45	53.329	533	400
178.35	101.325	1 013.25	760

Latent Heat of Vaporization @ 182.9 °K and 176 kPa 18.661 kJ/mol; 4.46 kcal/mol

Thermodynamic Properties of Silicon Tetrafluoride As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	73.492 J/(mol·°K)
Entropy, S°	282.140 J/(mol·°K)
Free Energy Function, $(F^\circ_{298} - H^\circ_{298})/298$	−282.140 J/(mol·°K)
Enthalpy Difference, $H^\circ_{298} - H^\circ_0$	15.309 kJ/mol
Enthalpy of Formation, ΔH_f°	−1 614.940 kJ/mol
Free Energy of Formation, ΔF_f°	−1 572.577 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of silicon tetrafluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*,, *2nd edition*, *1977*, pp. 83–87, Matheson, Lyndhurst, New Jersey.

[3] *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p. 3-48, McGraw-Hill Book Co., Inc., New York, New York.

[4] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[5] *The Sadtler Standard Spectra*, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

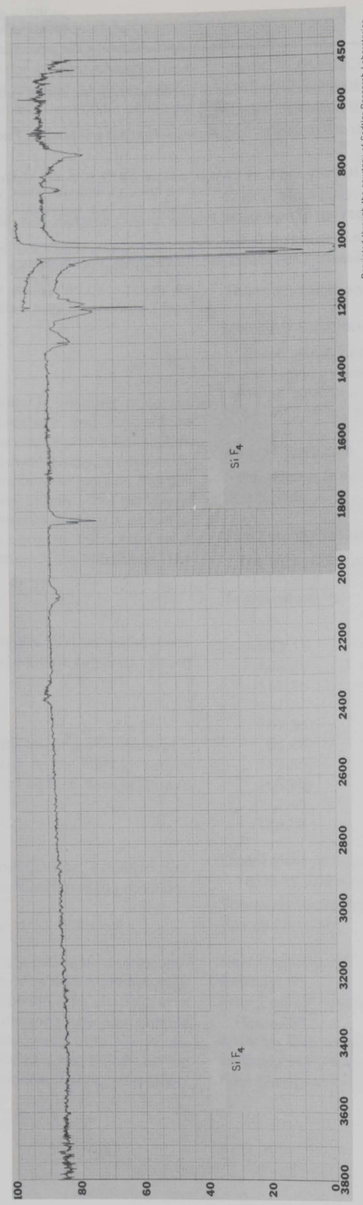


Fig. 2. Infrared spectrum of gaseous silicon tetrafluoride; 10 cm path length cell, with KBr windows; cell pressure: curve A (complete scan): 1.333 kPa (10 mmHg); curve B (partial scan): 0.066 7 kPa (0.5 mmHg) (5).

Matheson

SULFUR DIOXIDE

(Synonym: Sulfurous Acid Anhydride)
(Formula: SO_2)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.064 063 kg
One Mole of SO_2	0.064 063 kg
Specific Volume @ 2.1 °C, 101.325 kPa	368.3 dm^3/kg; 5.9 ft/lb
Vapor Pressure @ 21.1 °C	339 kPa; 3.39 bar; 49.1 psia; 3.34 atm
Boiling Point @ 101.325 kPa	263.134 °K; −10.0 °C; 14.0 °F
Triple Point	197.31 °K; −75.8 °C; −103.9 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	2.668 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	2.263
Density, Liquid @ −10.0 °C	1.462 kg/l
Critical Temperature	430.75 °K; 157.6 °C; 315.7 °F
Critical Pressure	7 884 kPa; 78.84 bar; 1 143.5 psia; 77.81 atm
Critical Volume	1.904 dm^3/kg
Critical Density	0.525 kg
Critical Compressibility Factor	0.268
Latent Heat of Fusion @ 197.31 °K	7.401 kJ/mol; 1.769 kcal/mol; 115.527 kJ/kg
Dipole Moment, Gas	5.34×10^{-30} C·m; 1.6 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant Pressure	39.884 J/(mol·°K)
@ Constant Volume	30.932 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.29
Specific Heat, Liquid @ 0 °C	1.331 kJ/kg
Viscosity, Gas @ 101.325 kPa @ 10 °C	0.012 00 mPa·s; 0.012 00 cP
Viscosity, Liquid @ 0 °C	−0.40 mPa·s; 0.40 cP
Thermal Conductivity @ 101.325 kPa @ 15 °C	0.008 8 W/(m·°K); 21.0×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −25 °C	0.221 4 W/(m·°K) 529×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −10 °C	28.59 mN/m; 28.59 dyn/cm
Solubility In Water @ 101.325 kPa (total pressure of SO_2 plus aqueous tension)	
@ 0 °C	22.83 kg SO_2/100 kg water
@ 20 °C	11.28 kg SO_2/100 kg water
Refractive Index, Gas @ 101.325 kPa, n_D @ 25 °C	1.000 602 2
Dielectric Constant, Gas @ 20 °C, 101.325 kPa	1.009 3
Dielectric Constant, Liquid @ 20 °C	14.1
Electrical Conductivity, Liquid	$80 \times 10^{-9}\ \Omega^{-1}$/cm

Description

At room temperature and atmospheric pressure, sulfur dioxide is a highly irritating, nonflammable, colorless, toxic gas. It is shipped in steel cylinders and ton containers as a liquefied compressed gas under its own vapor pressure of 237 kPa (34.4 psig) at 21.1 °C

Specifications

Matheson supplies an Anhydrous Grade of sulfur dioxide, with a minimum purity of 99.98%.

Uses

The uses of sulfur dioxide are many, some of which are as follows: as a preservative for beer, wine, and meats; in the

Matheson

manufacture of sulfite and hydrogen sulfites; in solvent extraction of lubricating oils, as a general bleaching agent of oils and foods; in sulfite pulp manufacture; in the cellulose and paper industries; as a refrigerant in the ice industry; in disinfecting and fumigation; in tanning.

Effects in Man and Toxicity (2)

Sulfur dioxide is a highly irritating gas; it readily elicits respiratory reflexes. It is intensely irritating to the eyes, throat, and respiratory tract. Inhalation of this gas in concentrations of 8–12 ppm in air causes throat irritation, coughing, constriction of the chest, and tearing and smarting of the eyes. A concentration of 150 ppm can be endured only a few minutes, because of eye irritation and the effect on the membranes of the nose, throat and lungs. Exposure to a concentration of 500 ppm by volume in air for a few minutes is very dangerous.

It is reported (Oct. 19, 1970 issue of Chem. & Eng. News, p. 71) that sulfur dioxide damages human white blood cells in tissue culture. When a concentration of 5.7 ppm of sulfur dioxide by volume in air is bubbled through cultures of lymphocytes, this causes fewer of the cells to synthesize DNA, divide, or grow. The cells are smaller than those grown in sulfur dioxide-free air, and about 20% of the cells have altered chromosome structures. It has also been found that animals exposed to sulfur dioxide become less resistant to microorganisms.

Liquid sulfur dioxide may cause skin and eye burns upon contact with these tissues, which results from the freezing effect of the liquid on the skin or eyes. Low (1%) concentrations of the vapor are irritating to moist skin within a period of 3 minutes.

The odor of sulfur dioxide provides good warning. The normal person can detect 3–5 ppm by volume in air. Low concentrations create a taste sensation, even before the odor becomes detectable.

Threshold Limit Value (TLV)

The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 5 ppm (13 mg/m^3) for sulfur dioxide.

First Aid Treatment (2)

Inhalation

Any worker who has been overcome by sulfur dioxide must be carried at once to an uncontaminated atmosphere, and effective artificial respiration started immediately if breathing has ceased. A physician should be called at once. For effective artificial respiration it is recommended that the Nielsen arm-lift back-pressure method, the Eve rocking method, or the Schafer prone-pressure method be applied. Pure oxygen should be administered as soon as possible after a severe exposure. Oxygen administration is most effective if expiration is made against a positive pressure of 4 cm (about 1¼ inches of water. This may be accomplished by use of a rubber tube connected to the outlet valve of a snugly fitting face mask and inserted to a depth of not more than 4 cm below the surface of water in a suitable container. (Special masks are obtainable with adjustable gauges which regulate the positive pressure from 1 to 4 cm). The pressure resisting exhalation should be adjusted to the victim's tolerance by varying the depth of the end of the tube below the water's surface. Oxygen inhalation must be continued as long as necessary to maintain the normal color of the skin and mucous membranes. In cases of severe exposure, the victim should breathe 100% oxygen under positive exhalation pressure for ½ hour every hour for at least 3 hours. If there are no signs of lung congestion at the end of this period, and if breathing is easy and the color is good, oxygen inhalation may be discontinued. Throughout this time, the victim should be kept comfortably warm, but not hot.

Skin Contact

The emergency safety shower should be used immediately. All contaminated clothing, including shoes should be removed under the shower. The sulfur dioxide should be washed off the affected skin areas with very large quantities of soap and water. No salves or ointments should be applied to chemical burns for 24 hours. A physician should see all cases other than minor burns.

Contact With Eyes

The eyes should be washed with copious quantities of water, followed by the introduction of saturated boric acid solution and by use of a local anesthetic, such as 0.5% pontocaine hydrochloride. These are followed by the application of olive oil or some similar oil. The victim should see a physician, preferably an eye specialist, at once.

Suggested Medical Treatment

Although stimulants will rarely be necessary where adequate oxygenation is maintained following a severe exposure, in some cases the use of respiratory and circulatory stimulants such as coramine, metrazol, and caffeine-sodium benzoate may be of value. A few days of absolute bed rest should be advised for those who have had a fairly severe exposure, and this should be continued until all evidence of respiratory embarrassment ceases. During this period codeine phosphate or sulfate, from ½ to 1 grain, every 4 to 6 hours, will alleviate the cough and may frequently be combined with a soothing cough-syrup mixture. For those who display symptoms of acute asthma, the subcutaneous administration of 0.5 to 1 ml of 1:1000 solution of adrenalin may relieve the symptoms. The use of a nebulizer for inhalation of 1:100 adrenalin might also be of value.

Precautions in Handling and Storage

Sulfur dioxide should be handled only in a well-ventilated area, preferably a hood with forced ventilation. Personnel handling sulfur dioxide should wear chemical safety goggles and/or plastic face shields, approved safety shoes, and rubber gloves. In an emergency, gas masks, approved by the U.S. Bureau of Mines for sulfur dioxide, should be worn, as required. Additional gas masks, air-line gas masks, and self-contained breathing apparatus should be conveniently located for use in emergencies. Instant-acting safety showers should be available in convenient locations. Since suckback may cause a violent reaction within the cylinder, a check valve, trap, or vacuum break should be employed when using sulfur dioxide.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks of sulfur dioxide in lines or equipment may be located by passing a squeeze bottle of aqueous ammonia over sites of suspected leaks; dense white fumes will be formed near the leak. Leaks may be less eaily located by applying oil or soap water solution to joints; leaks will be evident by bubble formation.

Analytical Detection

Numerous methods are available for the detection and estimation of sulfur dioxide. Eight procedures are described by Jacobs (3).

Matheson has available a Toxic Gas Detector Model 8014K as follows:

(1) Model 8014-103SA detector tube for detection of sulfur dioxide in the concentration range of 0.1-3.0%; (2) Model 8014–103SB detector tube for detection of sulfur dioxide in the concentration range of 0.02–0.3%; (3) Model 8014–103SC detector tube for detection of sulfur dioxide in the concentration range of 10–300 ppm; (4) Model 8014–103SD detector tube for detection of sulfur dioxide in the concentration range 1–30 ppm. A color stain is produced in a detector tube which varies in length according to concentration being measured. The length of the stain and hence concentration, is read directly off the detector tube.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-D.

Materials of Construction

Anhydrous sulfur dioxide, is noncorrosive to steel and other common structural metals, except zinc. In the presence of moisture, however, corrosive conditions will develop. Haveg, lead, carbon, graphite, aluminum, and stainless steel type 316 are recommended for handling moist sulfur dioxide.

Cylinder and Valve Description

Sulfur dioxide is shipped in DOT approved, high pressure steel cylinders. Cylinders of sulfur dioxide are equipped with brass valves with Compressed Gas Association (CGA) approved alternate valve outlet connection No. 660. The valve outlet has a thread size of 1.030 inches with right-hand external threads, with a flat seat and using a washer as a seal (see Figure 1 for an illustration). Lecture bottles have a special $^{5}/_{16}$ inch-32 threads per inch, female outlet.

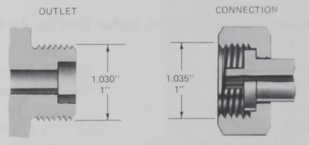


Fig. 1 CONNECTION 330 .825"-14 LH EXT. used with Flat Seat and Washer

Safety Devices

Cylinders of sulfur dioxides are equipped with fusible metal plugs, melting about 73.9 °C (165 °F), as safety devices. Cylinders over 30 inches long, exclusive of the neck, require this device in both ends of the cylinder. Cylinders of sulfur dioxide should, therefore, be stored away from sources of heat capable of melting the fusible metal.

Liquid sulfur dioxide may be removed by inverting or partly inverting the cylinder. To remove gaseous sulfur dioxide and increase its rate of flow and to protect the fuse plug, the cylinder should be heated, preferably in a warm booth or room or by immersing the cylinder in a warm liquid bath which does not cover more than half the lower end of the cylinder. In no case should the temperature of the room or bath be higher than 51.7 °C (125 °F).

Recommended Controls

Automatic Pressure Regulators

Regulator Model 13-660 is recommended for use with sulfur dioxide. The regulator has an anodized aluminum body with internal parts of type 316 stainless steel. The diaphragm is of FEP Teflon on Neoprene and the seat is of Teflon. The delivery pressure range is 28-240 kPa (4–35 psig). No cylinder pressure gauge is necessary since it will not indicate cylinder content but only vapor pressure, which will remain constant as long as liquid is present in the cylinder. Cylinder content is determined by weight. To prevent suckback of foreign materials, a stainless steel check valve (Model 401N) is recommended for use with the regulator.

For low pressure regulation, Matheson supplies a Model 71-660 regulator. This regulator has an oversize pancake body of aluminum with internal parts of type 303 stainless steel. It has a Teflon-faced Butyl rubber diaphragm and a Teflon seat. The delivery pressure range is 3.4–34.5 kPa (0.5–5.0 psig).

Manual Controls

Matheson needle valve Model 61–660, of type 303 stainless steel, is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets such as a hose connection, ¼" tube fitting, or ¼" NPT male or female pipe. It should be used only where manual flow control is needed and should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. Manual needle valve Model 32S is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings

are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Sulfur dioxide is classified by the DOT as a nonflammable compressed gas and is shipped with required "Green Label".

Commercial Preparations

Sulfur dioxide is produced by the combustion of sulfur in burners or special design, by burning pyrites, or as by-product of smelter operations. It can also be prepared by burning sulfur or a metallic sulfide in air, by the action of an acid on a metallic sulfide, or by the action of sulfuric acid on a metal below hydrogen in the electromotive series, e.g., $Cu + 2\ H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$.

Chemical Properties

Sulfur dioxide dissolves in water forming sulfuric acid, which is unstable toward heat. In many of its reactions, sulfur dioxide behaves as a reducing agent. Thus, permanganate, dichromate, iodate, the halogens, Fe^{3+}, and Hg_2^{2+} oxidize SO_2 to SO_4^{2-} in either dilute acid or neutral solution. In certain cases, SO_2 can act as an oxidizing agent. E.g., metals such as tin, iron, and magnesium burn in SO_2 to form mixed sulfides and oxides. In very strong acidic aqueous solutions, SO_2 can oxidize Fe^{2+}, Sn^{2+}, Cu^+, or Hg_2^{2+}, the reduction product being sulfur or a sulfide.

Liquid SO_2 is a poor solvent for most ionic compounds except iodides or bromides; tetraalkylammonium salts are very soluble. A wide variety of covalent compounds are soluble in SO_2, e.g., CCl_4, $SiCl_4$, $SnCl_4$, $TiCl_4$, CS_2, $(CH_3)_2O$, C_6H_6, C_6H_5Cl, alcohols, esters, ketones, and aldehydes.

Liquid SO_2 is a very poor conductor of electricity, in which respect it is similar to water.

Thermodynamic and Detailed Physical Data

Molecular Structure (4)

Sulfur dioxide is a bent triatomic molecule, with C_{2v} point symmetry and a symmetry number of two, with the following structural parameters: bond distance: S-O 1.432 Å (1.432×10^{-10} m); bond angle; O-S-O 119.53 °.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous sulfur dioxide.

Vapor Pressure (5)

Vapor pressure below 101.325 kPa are shown below.

	Vapor Pressure		
Temperature, °K	kPa	mbar	mmHg
177.65	0.133	1.33	1
190.15	0.667	6.67	5
196.35	1.333	13.3	10
203.45	2.666	26.7	20
212.65	5.333	53.3	40
218.55	7.999	80.0	60
226.25	13.332	133	100
237.75	26.664	267	200
250.15	53.329	533	400
263.15	101.325	1 013.25	760

For additional vapor pressure data below 101.325 kPa, see Table 1.

For vapor pressure data above 101.325 kPa, see below (6).

	Vapor Pressure		
Temperature, °K	kPa	bar	atm
263.15	101.325	1.013 25	1
279.45	202.650	2.03	2
305.25	506.625	5.07	5
328.65	1 013.250	10.1	10
356.95	2 026.500	20.3	20
375.75	3 039.750	30.4	30
391.15	4 053.000	40.5	40
403.35	5 066.250	50.7	50
414.85	6 079.500	60.8	60
430.35	7 872.952	78.7	77.7

For additional vapor pressure data above 101.325 kPa, see Table 1 and Figure 3.

Latent Heat of Vaporization, Δ Hv @ 263.15 °K 386.5 kJ/kg

For additional Δ Hv values, see Table 1.

Thermodynamic Data

Thermodynamic properties of saturated and superheated SO_2 are shown in Tables 1 and 2, respectively.

Thermodynamic Properties of Sulfur Dioxide As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	39.874 J/(mol·°K)
Entropy, S°	248.103 J/(mol·°K)
Free Energy Function, $(F^\circ_{298} - H^\circ_{298})/298$	−248.103 J/(mol·°K)
Enthalpy Difference, $H^\circ_{298} - H^\circ_0$	10.552 kJ/mol
Enthalpy of Formation, ΔH_f°	−296.842 kJ/mol
Free Energy of Formation, ΔF_f°	−300.164 kJ/mol

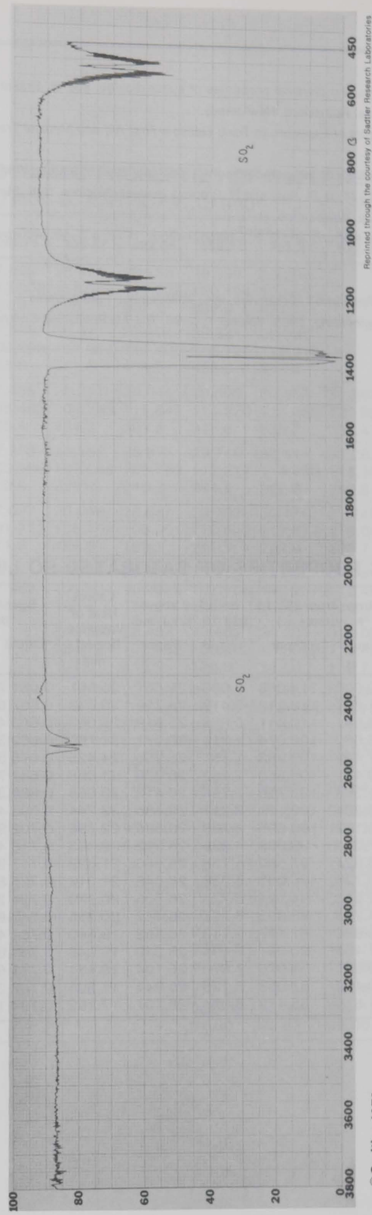


Fig. 2. Infrared spectrum of gaseous sulfur dioxide; 10-cm path length cell, with KBr windows; cell pressure (complete scan) 0.666 6 kPa (5 mmHg) (7).

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of sulfur dioxide, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 140–144, Matheson, Lyndhurst, New Jersey.

[3] M. B. Jacobs, The **Analytical Toxicology of Industrial Inorganic Poisons**, *1967*, pp. 528–539, John Wiley & Sons, Inc., New York, New York.

[4] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[5] *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p 3-48, McGraw-Hill Book Co., Inc., New York, New York.

[6] **Ibid.**, p. 3-45.

[7] *The Sadtler Standard Spectra*, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[8] W. R. Woolrich, *Handbook of Refrigerating Engineering*, *1965*, Volume 1, p. 96, The Avi Publishing Company, Inc., Westport, Connecticut.

[9] **Ibid.**, p. 100.

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED SO LIQUID AND VAPOR (8)

Temperature		Pressure		Entropy from 233.15 °K J/(mol·°K)		Enthalpy above 233.15 °K kJ/mol		Latent Heat of Vaporization kJ/mol	Specific Volume dm³/kg		Density kg/dm³	
°K	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
233.15	−40	21.622	0.213	0.000	114.083	0.000	25.567	25.567	0.651 7	1 399.6	1.534	0.000 71
238.71	−30	29.861	0.295	1.807	112.212	0.419	25.752	25.333	0.657 5	1 033.8	1.521	0.000 97
244.26	−20	40.562	0.400	3.661	110.411	0.856	25.919	25.063	0.663 4	775.4	1.507	0.001 29
249.82	−10	54.213	0.535	5.562	108.674	1.311	26.071	24.760	0.669 3	589.3	1.494	0.001 70
255.37	0	71.361	0.704	7.492	106.993	1.781	26.206	24.425	0.675 5	454.5	1.480	0.002 20
260.93	10	92.528	0.913	9.432	105.356	2.262	26.320	24.058	0.681 7	354.7	1.467	0.002 82
266.48	20	118.452	1.169	11.368	103.750	2.748	26.413	23.665	0.688 3	280.1	1.453	0.003 57
272.04	30	149.616	1.477	13.284	102.174	3.241	26.485	23.244	0.695 4	223.6	1.438	0.004 47
277.59	40	186.848	1.844	15.192	100.625	3.739	26.535	22.796	0.702 9	180.2	1.423	0.005 55
283.15	50	230.630	2.276	17.074	99.092	4.239	26.562	22.323	0.710 4	148.6	1.408	0.006 73
288.71	60	282.202	2.785	18.924	97.580	4.738	26.566	21.828	0.717 9	120.3	1.393	0.008 31
294.26	70	342.118	3.376	20.736	96.081	5.236	26.548	21.312	0.725 8	99.26	1.378	0.010 08
299.82	80	411.479	4.061	22.513	94.594	5.733	26.506	20.773	0.734 2	82.47	1.362	0.012 13
305.37	90	491.251	4.848	24.225	93.093	6.227	26.442	20.215	0.742 6	68.92	1.347	0.014 51
310.93	100	582.745	5.751	25.885	91.597	6.713	26.353	19.640	0.751 4	57.82	1.331	0.017 30
316.48	110	687.821	6.788	27.485	90.091	7.194	26.240	19.046	0.761 0	48.72	1.314	0.020 52
322.04	120	833.783	8.229	29.026	88.576	7.670	26.104	18.434	0.771 6	41.19	1.296	0.024 28
327.59	130	940.996	9.287	30.492	87.038	8.138	25.944	17.806	0.782 2	34.93	1.278	0.028 63
333.15	140	1 093.577	10.793	31.878	85.472	8.594	25.757	17.163	0.794 1	29.70	1.259	0.033 67

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED SULFUR DIOXIDE (9)

H, ENTHALPY, kJ/mol; **S**, ENTROPY, J/(mol·°K); **V**, SPECIFIC VOLUME, dm³/kg

Pressure			Temperature, °K										
kPa	atm		272.04	288.71	305.37	322.04	338.71	355.37	372.04	388.71	405.37	422.04	438.71
68.948	0.680	H	26.969	27.699	28.429	29.159	29.889	30.604					
		S	110.322	113.008	115.536	117.929	120.194	122.363					
		V	501.3	541.9	575.2	607.8	639.9	671.7					
103.421	1.02	H	26.811	27.598	28.371	29.101	29.831	30.561					
		S	106.337	109.299	111.947	114.405	116.726	118.918					
		V	332.9	358.0	381.6	404.0	425.8	447.4					
137.895	1.36	H		27.455	28.271	29.044	29.803	30.533	31.263				
		S		106.463	109.248	111.842	114.220	116.461	120.320				
		V		265.4	284.2	301.8	318.6	335.2	351.4				
172.369	1.70	H		27.283	28.157	28.973	29.746	30.518	31.263	21.993			
		S		103.986	107.068	109.760	112.217	114.498	116.364	118.675			
		V		209.9	225.9	240.2	254.3	267.6	280.8	293.8			
206.843	2.04	H		27.097	28.042	28.887	29.703	30.476	31.249	32.007			
		S		101.772	105.409	108.001	110.542	112.877	115.045	117.109			
		V		171.5	186.0	199.1	211.1	222.6	233.7	244.7			
275.290	2.72	H		26.611	27.713	28.686	29.559	30.390	31.191	31.821			
		S		97.952	101.834	105.026	107.776	110.237	112.485	114.590			
		V		123.6	136.4	147.3	157.0	166.2	174.8	183.1			
344.738	3.40	H			27.369	28.457	29.402	30.289	31.105	31.921	32.709		
		S			98.872	102.482	105.482	108.092	110.432	112.617	114.697		
		V			107.6	116.9	125.0	132.5	139.7	146.5	153.2		
413.685	4.08	H				28.200	29.230	30.161	31.034	31.864	32.666	33.467	
		S				100.180	103.471	106.248	108.701	110.944	113.046	115.083	
		V				87.59	97.57	105.4	111.434	117.7	123.5	12.92	
482.633	4.76	H				27.885	29.044	30.046	30.934	31.792	32.623	33.424	
		S				97.955	101.579	104.573	107.157	109.481	111.647	113.697	
		V				79.41	86.71	92.96	98.64	103.9	108.9	113.9	
551.581	5.44	H				27.555	28.815	29.874	30.848	31.721	32.580	33.410	
		S				95.950	99.898	103.091	105.798	108.205	110.419	113.507	
		V				67.67	74.85	80.66	85.78	90.58	95.14	99.45	
689.476	6.80	H				26.811	28.328	29.545	30.604	31.563	32.465	33.324	
		S				91.927	96.658	100.330	103.345	105.940	108.280	110.451	
		V				51.13	57.78	63.18	67.80	71.92	75.73	79.16	
827.371	8.17	H					27.756	29.159	30.347	31.392	32.336	33.238	34.111
		S					93.557	97.818	101.150	103.959	106.447	108.711	110.802
		V					46.22	51.37	55.66	59.40	62.80	65.92	68.92
965.266	9.53	H					27.155	28.744	30.060	31.191	32.193	33.138	34.026
		S					90.536	95.390	99.110	102.171	105.629	107.176	109.336
		V					37.80	42.83	46.90	50.38	53.46	56.29	58.94

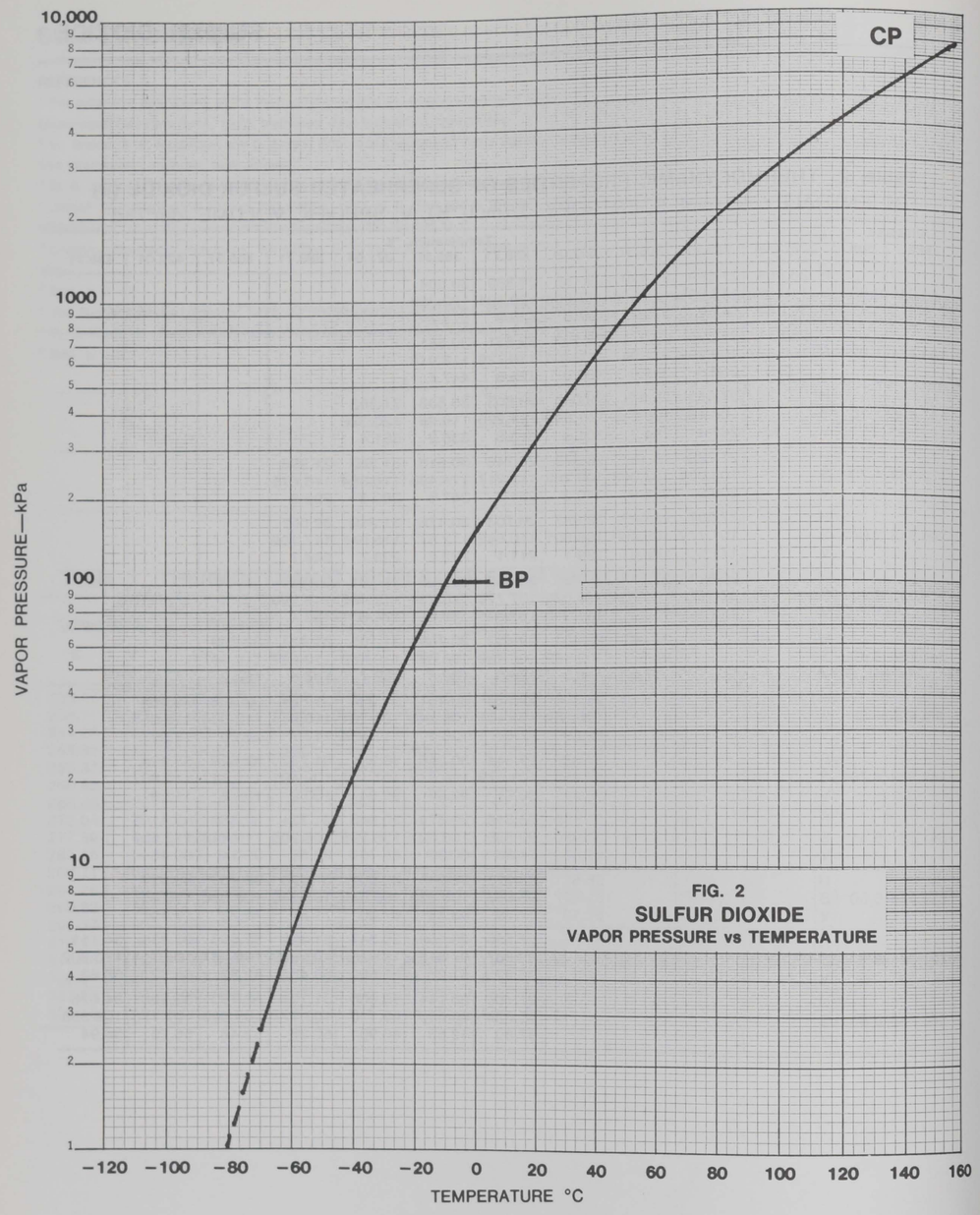


FIG. 2
SULFUR DIOXIDE
VAPOR PRESSURE vs TEMPERATURE

SULFUR HEXAFLUORIDE

(Formula: SF_6)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.146 054 kg
One Mole of SF_6	0.146 054 kg
Specific Volume @ 21.1 °C, 101.325 kPa	156.1 dm^3/kg; 2.5 ft^3/lb
Vapor Pressure @ 21.1 °C	2 308 kPa; 23.08 bar; 334.7 psia; 22.77 atm
Sublimation Point @ 101.325 kPa	209.45 °K; −63.7 °C; −82.7 °F
Melting Point @ 224 kPa	222.35 °K; −50.8 °C; −59.4 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	6.162 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	5.114
Density, Liquid @ Saturation Pressure @ −50 °C	1.91 kg/l
Critical Temperature	318.69 °K; 45.5 °C; 114.0 °F
Critical Pressure	3 759 kPa; 37.59 bar; 545.2 psia; 37.1 atm
Critical Volume	1.356 dm^3/kg
Critical Density	0.736 kg/dm^3
Critical Compressibility Factor	0.267
Heat of Sublimation @ 209.45 °K	23.598 kJ/mol; 5 640 cal/mol
Latent Heat of Fusion @ 222.35 °K, 224 kPa	5 020.8 J/mol; 1 200 cal/mol
Dipole Moment, Gas	0 C·m
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	97.152 J/(mol·°K)
Molar Specific Heat, Liquid @ 225 °K	110.876 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.015 6 mPa·s; 0.015 6 cP
Viscosity, Liquid @ 229.85 °K	0.500 mPa·s; 0.500 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 30 °C	0.014 06 W/(m·°K); 33.6×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −50 °C	11.63 mN/m; 11.63 dyn/cm
Solubility In Water @ Partial Pressure of SF_6 of 101.325 kPa @ 25 °C	5.4 cm^3 SF_6/kg water
Index of Refraction, Gas @ 101.325 kPa, n_D @ 0 °C	1.000 783
Dielectric Constant, Gas @ 101.325 kPa @ 25 °C	1.002 049
Velocity of Sound in SF_6 @ 30 °C	138.4 m/s

Description

At room temperature and atmospheric pressure, sulfur hexafluoride is a colorless, odorless, nontoxic gas. It is readily liquefied and is shipped in steel cylinders as a liquefied gas under its own vapor pressure of 2 210 kPa (320 psig) at 21.1 °C.

Specifications

Matheson supplies two grades of sulfur hexafluoride.

1. Instrument Purity Grade

This grade has a minimum purity of 99.99 mole % in the liquid phase.

2. C.P. Grade

This grade has a minimum purity of 99.8 mole % in the liquid phase.

Uses

Sulfur hexafluoride is used chiefly as an insulating medium for a wide range of high voltage electrical and electronic equipment.

Effects In Man and Toxicity (2)

Sulfur hexafluoride has a low order of inhalation toxicity. The 1979 ACGIH has recommended a Threshold Limit Value of 1 000 ppm for sulfur hexafluoride. Sulfur hexafluoride can, however, act as a simple asphyxiant by displacing the necessary amount of oxygen to support life.

The coordinating capacity of the nervous system is impaired by even slight degrees of oxygen deficiency; the subject can not think clearly or control his limbs accurately. The development of symptoms depends on the degree and duration of the oxygen deficiency and also on the rapidity with which the deficiency is developed. In sudden and acute asphyxia, unconsciousness is immediate. When asphyxia develops slowly

enough the following symptoms appear: increased volume of breathing, accelerated pulse rate, muscular incoordination, faulty judgment, emotional instability, fatigue, fainting, nausea, vomiting, disorientation, respiration in gasps.

Inhalation of gaseous decomposition products of sulfur hexafluoride resulting from electrical decomposition should be avoided.

First Aid Treatment (2)

If the subject is conscious and becomes aware of symptoms of asphyxia, he should go to an uncontaminated area and inhale fresh air or oxygen.

An unconscious subject must be carried to an uncontaminated area and given artificial respiration with simultaneous administration of oxygen as promptly as possible.

Few, even those who have been severely asphyxiated and who have not died during the asphyxiation, fail to make complete recoveries after receiving oxygen inhalation. Treat symptomatically thereafter.

Precautions in Handling and Storage

The general rules stated in Appendix I should be observed.

Leak Detection

Leaks of sulfur hexafluoride in lines of equipment may be detected by painting the sites of the suspected leaks with soap water solution; leaks will be evident by bubble formation. Minute leaks in pressurized equipment filled with sulfur hexafluoride may be detected with either a halide torch or a halide leak detector. A more sensitive means of leak detection is provided by the Matheson Models 8016 and 8017 Leak Detectors.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-C.

Materials of Construction

Since sulfur hexafluoride is noncorrosive, any of the common structural metals may be used under ordinary conditions. At temperatures of the order of 150 °C copper, stainless steel, and aluminum are resistant to attack by decomposition products.

Cylinder and Valve Description

Sulfur hexafluoride is shipped in DOT approved, high pressure steel cylinders. Cylinders of sulfur hexafluoride are equipped with brass valves having Compressed Gas Association (CGA) valve outlet connection No. 590. The valve outlet has a thread size of 0.965 inch, with left-hand internal threads accepting a bullet-shaped nipple (see Figure 1 for an illustration). Lecture bottles have a special 5/16"-32 threads per inch, female outlet and a 9/16"-18 threads per inch, male dual valve outlet.

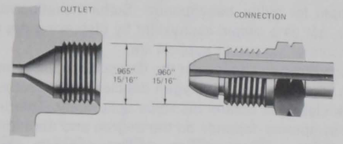


Fig. 1 CONNECTION 590 .965"-14 LH INT. accepting a Bullet Shaped Nipple

Safety Devices

Cylinders of sulfur hexafluoride are equipped with frangible discs as safety devices. The frangible disc is required in only one end of the cylinder regardless of the length of the cylinder. Cylinders of sulfur hexafluoride should, therefore, be stored away from sources of heat to avoid dangerous pressures from developing within the cylinder. Frangible discs backed up with fusible metal plugs, melting at about 73.9 °C (165 °F) or 100 °C (212 °F), may also be used as safety devices, but in cylinders over 55 inches long, exclusive of the neck, this device is required in both ends.

Recommended Controls

Automatic Pressure Regulators

In order to reduce the cylinder pressure of sulfur hexafluoride to a safe working value consistent with a system's design, the following automatic regulators are recommended for use.

1. Single Stage Regulator

A single stage regulator will reduce cylinder pressure in one stage to a delivery pressure in a particular range depending upon the design of the regulator and its spring load. A single stage regulator will show a slight variation in delivery pressure as the cylinder pressure falls. The following single stage regulators are available from Matheson for use with C.P. Grade sulfur hexafluoride.

Model No.	Delivery Pressure Range kPa	bar (g)	psig
1P-590	28–240	0.28–2.4	4–35
1L-590	28–550	0.28–5.5	4–80
1H-590	69–1 240	0.69–12.4	10–180

The following single stage high purity regulators are available for use with Instrument Purity Grade sulfur hexafluoride.

Model No.	Delivery Pressure Range kPa	bar (g)	psig
19-590	28–345	0.28–3.45	4–50
3500-590	28–520	0.28–5.2	4–75

Regulator Model 3321, with a delivery pressure range of 28–410 kPa (4–60 psig), is available for use with lecture bottles of either grade of sulfur hexafluoride.

2. Two Stage Regulators

This type of regulator performs the same function as the single stage regulator. However, greater accuracy and control of delivery pressure is maintained, and the delivery pressure does not vary as the cylinder pressure falls. The following two stage regulators are available from Matheson for use with C.P. Grade sulfur hexafluoride.

Model No.	Delivery Pressure Range kPa	bar (g)	psig
8L-590	14–104	0.14–1.04	2–15
8-590	28–345	0.28–3.45	4–50
8H-590	69–690	0.69–6.9	10–100
9-590	38–1 720	1.38–17.2	20–250

The following two stage regulators are available for use with Instrument Purity Grade sulfur hexafluoride.

Model No.	Delivery Pressure Range kPa	bar (g)	psig
3800-590	28–620	0.28–6.2	4–90
3104-590	28–690	0.28–6.9	4–100

Manual Controls

Matheson needle valve Model 50-590, of brass bar stock, is available for direct attachment to the cylinder valve outlet of C.P. Grade sulfur hexafluoride cylinders. This valve may be equipped with a variety of outlets, such as a hose connection, a ¼" tube fitting, or ¼" NPT male or female pipe.

Manual control Model 4351-590 is recommended for use with Instrument Purity Grade sulfur hexafluoride.

Needle valve Model 31B is available for use with either grade of sulfur hexafluoride.

Flowmeters

Matheson Series 7600 laboratory brass or stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass or stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Sulfur hexafluoride is classified by the DOT as a nonflammable compressed gas and is shipped with the required "Green Label."

Commercial Preparations

Sulfur hexafluoride is manufactured by passing fluorine over coarse sulfur, followed by several purification steps.

Chemical Properties

Sulfur hexafluoride is an unreactive substance. Sulfur hexafluoride is not attacked by water, acids, or bases, at room temperature. It is resistant to the action of carbon, copper, or magnesium at red heat, and will not react with sodium below its boiling point. It reacts with sulfur vapor or hydrogen at 400 °C.

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

Sulfur hexafluoride is an octahedral molecule, with O_h point group symmetry and a symmetry number of twenty-four. The structural parameters are as follows: S—F bond length: 1.564 Å (1.564×10^{-10} m); F—S—F bond angle: 90°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous sulfur hexafluoride.

Sublimation and Vapor Pressure (4)

Sublimation and vapor pressures of sulfur hexafluoride over several ranges are represented by the following equations:

Temperature Range, °K	Equation (T = °K)
83.15–193.15	$\log_{10}$ pmmHg = 2.787 5-624.29/T + 0.014 731 T
175.15–207.15	$\log_{10}$pmmHg = 8.711-1 222/T
201.15–227.15	$\log_{10}$pmmHg = 8.764 8-1 231.3/T
222.35–318.75	$\log_{10}$patm = 4.357 1-889.85/T

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv (4)

Temperature, °K	ΔHv, kJ/mol
222.35	18.828
233.15	17.908
253.15	15.439

Thermodynamic Properties of Sulfur Hexafluoride As Ideal Gas @ 25 °C (3)

Heat Capacity, C_p°	97.169 J/(mol·°K)
Entropy, S°	291.679 J/(mol·°K)
Free Energy Function, $(F^\circ_{298} - H^\circ_{298})/298$	−291.679 J/(mol·°K)
Enthalpy Difference, $H^\circ_{298} - H^\circ_0$	16.958 kJ/mol
Enthalpy of Formation, ΔH_f°	−1 220.849 kJ/mol
Free Energy of Formation, ΔF_f°	−1 116.986 kJ/mol

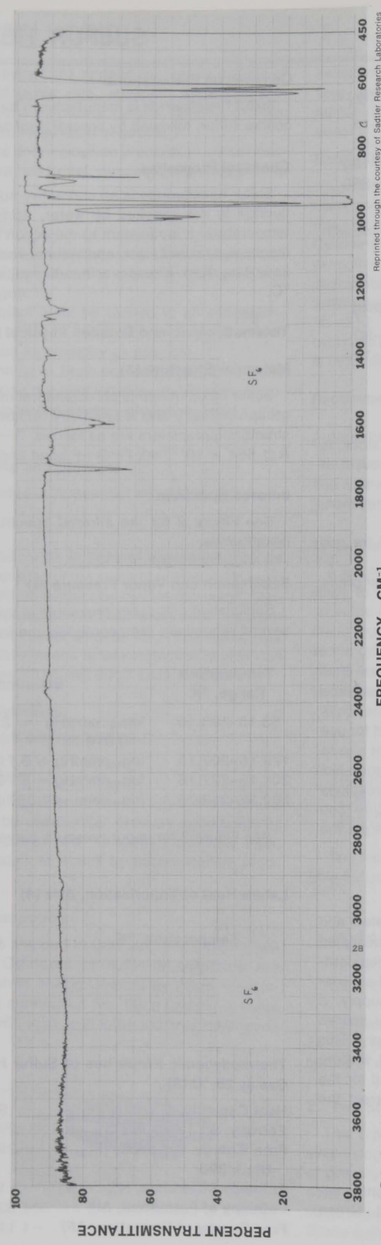


Fig. 2. Infrared spectrum of sulfur hexafluoride; 10-cm path length cell, with KBr optics; cell pressure: curve A (complete scan) 2.666 kPa (20 mmHg); curve B (partial scan) 0.0667 kPa (0.5 mmHg) (5).

Matheson

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of sulfur hexafluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, 138–140, Matheson, Lyndhurst, New Jersey.

[3] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[4] J. A. Brown in Kirk-Othmer's *Encyclopedia of Chemical Technology*, 2nd edition, *1966*, Volume 9, pp. 664–671, John Wiley & Sons, Inc., New York, New York.

[5] *The Sadtler Standard Spectra*, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Matheson

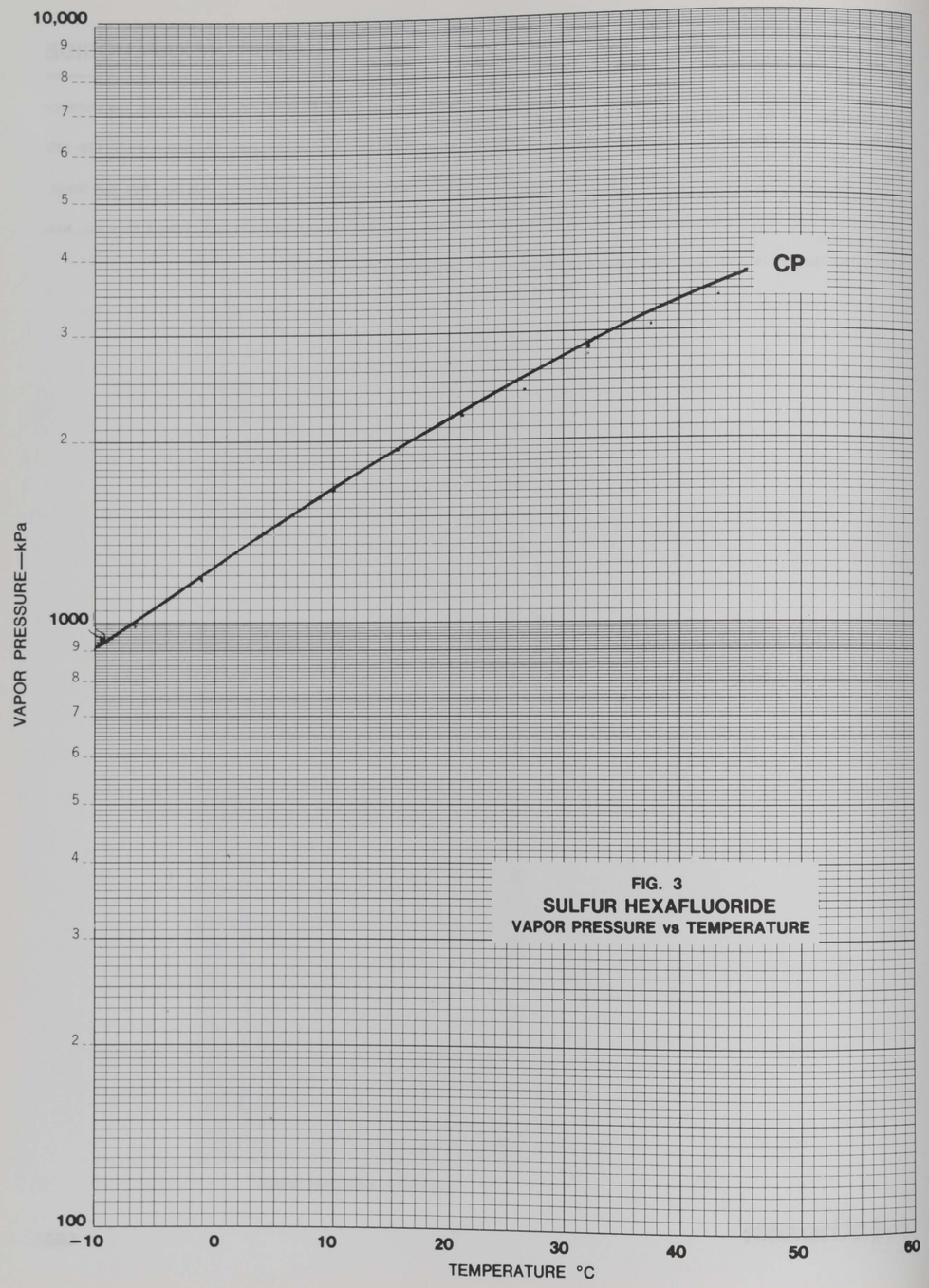


FIG. 3
SULFUR HEXAFLUORIDE
VAPOR PRESSURE vs TEMPERATURE

SULFUR TETRAFLUORIDE

(Formula: SF_4)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.108 058 kg
One Mole of SF_4	0.108 058 kg
Specific Volume @ 21.1 °C, 101.325 kPa	224.7 dm^3/kg; 3.6 ft^3/lb
Vapor Pressure @ 21.1 °C	1 067 kPa; 10.67 bar; 154.7 psia; 10.53 atm
Boiling Point @ 101.325 kPa	232.75 °K; −40.4 °C; −40.7 °F
Melting Point	152.65-151.65 °K; −120.5 to −121.5 °C; −184.9 to 186.7 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	4.558 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	3.783
Density, Liquid @ Saturation Pressure @ −80 °C	1.940 6 kg/l
Critical Temperature	364.05 °K; 90.9 °C; 195.6 °F
Dipole Moment, Gas	2.108×10^{-30} C·m; 0.632 D
Surface Tension @ 232.75 °K	19.85 mN/m; 19.85 dyn/cm
Trouton Constant	27.1

Description

Sulfur tetrafluoride is a highly reactive, colorless, highly toxic and corrosive gas, having an odor resembling that of sulfur dioxide. It is very readily hydrolyzed by moisture, leading to the formation of hydrofluoric acid and thionyl fluoride. It is shipped in cylinders as a liquefied compressed gas under its own vapor pressure of 965 kPa (140 psig) at 21.1 °C.

Specifications

Sulfur tetrafluoride as currently supplied by Matheson has a purity range of from 90–94 mole %.

Uses

Sulfur tetrafluoride is a reactive gas, capable of replacing oxygen in many organic, inorganic and organometallic compounds with fluorine. Thus, it is now possible to prepare a wide range of fluorinated products unavailable by practical routes.

Toxicity

Sulfur tetrafluoride is a highly toxic gas, which was found to be lethal to 1 of 2 animals exposed four hours to a nominal concentration of 50 ppm. All animals, even those exposed to 10 ppm for one hour, showed irregular breathing and signs of irritation. At higher concentrations, the clinical signs were severe and consisted of rapid labored breathing, weakness, cyanosis, and discharges from the nose. Animals receiving lethal amounts showed pulmonary edema on autopsy.

The 1979 ACGIH has recommended a Threshold Limit Value (TLV) of 0.1 ppm (0.4 mg/m^3) for sulfur tetrafluoride.

Sulfur tetrafluoride liberates hydrofluoric acid on exposure to moisture and will cause burns on unprotected skin areas.

The odor of sulfur tetrafluoride is detectable at low concentrations, but the odor perception level has not been determined. Desensitization to the detection of traces of sulfur tetrafluoride is also possible but has not been investigated.

First Aid Suggestions

Since exposure to sulfur tetrafluoride will result in hydrolysis to hydrogen fluoride, the first aid measures suggested for hydrogen fluoride exposure are recommended for use.

Summon a physician immediately for anyone who has been exposed to sulfur tetrafluoride. Prior to the physician's arrival, first aid must be started at once. The first aid suggestions which follow are those believed to be common practice in industry. Their adoption in any specific case should be subject to prior endorsement by a competent medical advisor.

Speed in removing the victim from the contaminated atmosphere and in removing sulfur tetrafluoride from the skin or eyes is of primary importance. All affected persons should be referred to a physician, even when the injury seems slight, and the physician should be given a detailed account of the accident.

Skin Contact

Anyone who has had contact with sulfur tetrafluoride should be subjected immediately to a drenching shower of water. The clothing should be removed as rapidly as possible, even while the victim is in the shower, and medical assistance obtained at once. It is essential that the exposed area be washed with copious quantities of water for a sufficient period of time to remove all sulfur tetrafluoride from the skin. The exposed areas of the skin should then be flushed with 2–3% aqueous ammonia, followed by liberal rinses of fresh water. After this, an ice-cold saturated solution of magnesium sulfate (Epsom salt) in 70% alcohol should be applied for at least 30 minutes. If the burn is in an area that cannot be immersed, then the area should be treated with the iced alcohol or the iced magnesium sulfate solution by applying saturated compresses, which should be changed every two minutes. The physician should be available by then to administer further treatment. If the physician is not yet available, it is then permissible to apply a generous quantity of a thick magnesia paste prepared from

powdered magnesium oxide, U.S.P., and glycerin, U.S.P. Oils and greases should not be applied except under instructions from a physician.

Always have on hand a supply of magnesia paste.

Eye Contact

If the eyes have been exposed to sulfur tetrafluoride, they should be irrigated immediately with copious amounts of clean water for a minimum of 15 minutes. The eyelids should be held apart during the irrigation to insure contact of the water will all tissues and surfaces of the eyes and lids. A physician, preferably an eye specialist, should be called at once. If a physician is not immediately available, instill one or two drops of 0.5% pontocaine solution, or an equally effective aqueous topical anesthetic, followed by a second irrigation with water, for 15 minutes. No oils or oily ointments should be instilled unless requested by a physician.

Inhalation

Anyone suspected of exposure to sulfur tetrafluoride should be carried into an uncontaminated atmosphere at once. Even in the absence of symptoms, the victim must not be permitted to return to work for at least 24 hours after exposure, because of the potential danger of developing edema of the lungs. A physician should be called immediately. The administration of 100% oxygen should be started as soon as possible after exposure, by trained personnel, and continued as long as is necessary to maintain the normal color of the skin and mucous membranes. In cases of severe exposure, the victim should breathe 100% oxygen under positive (4 cm) exhalation pressure for one-half hour periods every hour for at least three and preferably six hours. If there are no signs of lung congestion at the end of this period, and if breathing is easy and the color good, oxygen inhalation may be discontinued. Throughout this period, the victim should be kept comfortably warm but not hot. Under no circumstances should a patient be permitted to return home or back to work until examined and discharged by a physician who is aware of the nature of his exposure.

Precautions in Handling and Storage

1. Employees should be instructed to avoid contact with sulfur tetrafluoride and trained in the appropriate procedures in case of contact.
2. Adequate emergency showers and wash-up facilities should be available in areas where sulfur tetrafluoride is used.
3. Eye-washing fountains should be placed in accessible locations.
4. Hose masks, air-line masks, or self-contained breathing apparatus should be conveniently located in case of emergency, but in areas not likely to become contaminated.
5. Workers handling sulfur tetrafluoride should use full coverage of clothing at all times, rubber shoes soled with neoprene or an equally resistant material or rubbers made of the same materials, a hat or protective head covering, a full face mask and/or chemical goggles with plastic lenses, and gauntlet-type gloves made of neoprene, plasticized polyvinyl chloride, or an equally resistant material.
6. Leaking cylinders should be removed to the outdoors or to an isolated, well-ventilated area, and the contents transferred to other suitable containers, or disposed of in a safe manner.
7. Waste disposal of sulfur tetrafluoride, and materials containing it, depends to a great extent upon local conditions. All local, state, and federal regulations regarding health and pollution must be followed.
8. To prevent suckback of liquids into the cylinder, a check valve or trap should be inserted between the liquid and cylinder.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Equipment to contain sulfur tetrafluoride should be pretested for leaks with dry compressed air or an inert gas such as nitrogen. Small leaks of sulfur tetrafluoride may be detected by holding an open bottle of concentrated aqueous ammonia near the suspected site of the leak; leaks will be evident by the formation of dense white fumes. Leaks at the cylinder valve may be eliminated by tightening the stem, packing nut, or outlet cap.

Disposal of Leaking Cylinders

Leaking cylinders of sulfur tetrafluoride that cannot be corrected by ordinary methods may be disposed of by the procedure described in Appendix II-D.

Materials of Construction

Stainless steel or "Hastelloy C" lined containers have been used satisfactorily with sulfur tetrafluoride. Glass containers may be used for brief exposure to sulfur tetrafluoride provided moisture is removed by baking and is carefully excluded, but in the presence of trace amounts of moisture, glass is not suitable.

At low pressure, satisfactory flexible connections may be made with "Tygon" or surgical rubber tubing. Copper tubing has proved satisfactory for high pressure transfer of sulfur tetrafluoride at room temperature.

Cylinder and Valve Description

Sulfur tetrafluoride is shipped in DOT approved, low pressure, steel cylinders. Cylinders of sulfur tetrafluoride are equipped with steel valves with Compressed Gas Association (CGA) connection No. 330. The valve outlet has a thread size of 0.825 inch, with left-hand external threads, with a flat seat using a washer to seal, (see Figure 1 for an illustration of the valve outlet and its mating connection). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet.

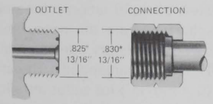


Fig. 1. CONNECTION 330 .825"-14 LH EXT. used with Flat Seat and Washer

Safety Devices

Cylinders of sulfur tetrafluoride contain safety devices which consist of frangible discs backed up with fusible metal, melting

at about 73.9 °C (165 °F). Cylinders should be stored away from sources of heat to prevent dangerous pressures from developing within the cylinder.

Recommended Controls

Automatic Pressure Regulators

Regulator Model B15-330, with a delivery pressure range of 28–345 kPa (4-50 psig) is recommended for use with sulfur tetrafluoride. It has a chemically-deposited pure nickel or brass body, a chemically-deposited pure nickel on nickel-silver alloy diaphragm, Kel-F seat, internal parts of monel, and a monel needle valve outlet with ¼" NPT male pipe.

Manual Controls

Manual needle valve Model 55-330, of monel bar stock, is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets (¼" tube fitting or ¼" male or female NPT pipe or a hose connection). It should be used only for manual flow control. It should not be used as a pressure control since it will not prevent pressure from building up if the system becomes clogged or if the system itself is closed. Needle valve Model 60L is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory monel flowmeter units with 150 mm tubes and floats are recommended for use where definite flow rates must be known.

Monel electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8260 of monel is designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/ power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Sulfur tetrafluoride is classified by DOT as nonflammable compressed gas and is shipped with the required "Green Label."

Chemical Preparation

Sulfur tetrafluoride has been prepared (a) by the spontaneous reaction of sulfur with cobalt trifluoride, mixed with calcium fluoride to moderate the reaction, (b) by fluorinating sulfur by means of fluorine diluted with nitrogen, (c) by pyrolysis of trifluoromethylsulfur pentafluoride and (d) by reacting sulfur dichloride with sodium fluoride suspended in acetonitrile at about 75 °C.

Chemical Properties

Sulfur tetrafluoride is thermally stable up to 600 °C. It is readily hydrolyzed by water yielding hydrofluoric acid and thionyl fluoride, the latter hydrolyzing slowly to hydrofluoric acid and sulfur dioxide. Sulfur tetrafluoride reacts with a wide variety of products forming selectively fluorinated products, e.g., it replaces carbonyl oxygen with fluorine in compounds like ketones, aldehydes, and quinones. It converts a carboxylic acid, or its ester, chloride, anhydride, or amide to a trifluoromethyl group without generally affecting olefinic and acetylenic bonds or other functional groups like fluoro, chloro, bromo, nitro, etc. It converts P=O and P(O)-OH groups into PF_2 and PF_3 groups, respectively. Sulfur tetrafluoride acts as an electron pair donor with Lewis acids, forming such donor-acceptor complexes as $SF_4 \cdot SbF_5$, $SF_4 \cdot PF_5$, $SF_4 \cdot AsF_3$, and $2SF_4 \cdot GeF_4$.

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

The molecule of sulfur tetrafluoride is a trigonal bipyramid, having C_{2v} point group symmetry and a symmetry number of two. The structural parameters are as follows: S-F bond distances of 1.545 Å (1.545×10^{-10} m) and 1.646 Å (1.646×10^{-10} m); F-S-F bond angles of 101.55° and 186.93°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous sulfur tetrafluoride.

Vapor Pressure (4)

The vapor pressure of liquid SF_4 between 163.15 and 223.15 °K is represented by the following equation:

$$\log_{10} p = 8.812\,6 - \frac{1\,381}{T}$$

in which p = mmHg and T = °K.

Latent Heat of Vaporization (4) @ 232.75 °K	26.443 kJ/mol (6.320 kcal/mol)

Thermodynamic Properties of Sulfur Tetrafluoride As Ideal Gas @ 25 °C (3)

Heat Capacity, C_p°	76.442 J/(mol·°K)
Entropy, S°	300.533 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−300.533 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	15.765 kJ/mol
Enthalpy of Formation, ΔH_f°	−780.734 kJ/mol
Free Energy of Formation, ΔF_f°	−739.949 kJ/mol

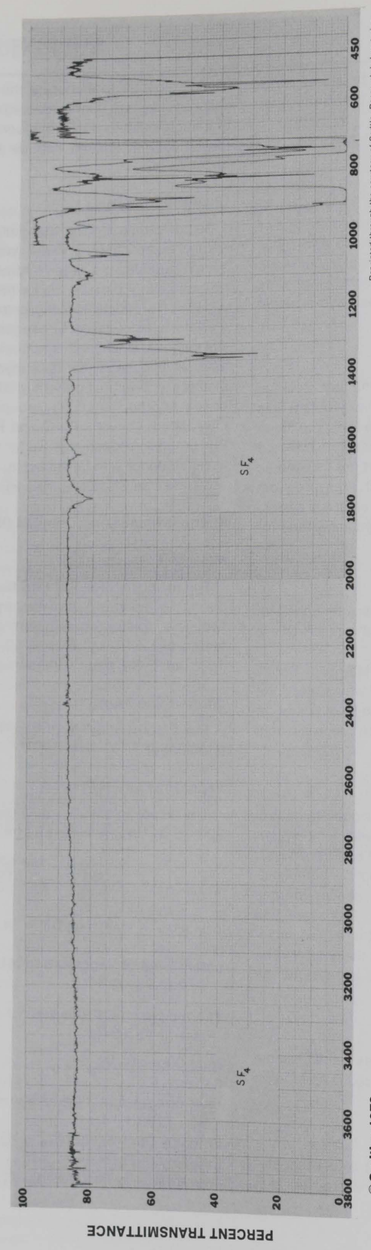


Fig. 2. Infrared spectrum of gaseous sulfur tetrafluoride; 10-cm path length cell, with KBr windows; cell pressure: Curve A (complete scan): 1.333 kPa (10 mmHg); curve B (partial scan): 0.066 7 kPa (0.5 mmHg) (5).

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of sulfur tetrafluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] *Information Bulletin*, E. I. duPont de Nemours & Co., Organic Chemicals Department, Dyes and Chemicals Division, Wilmington, Delaware.

[3] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[4] F. B. Brown and P. L. Robinson, *J. Chem. Soc.* (1955) 3147.

[5] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

SULFURYL FLUORIDE

(Formula: SO_2F_2)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.102 06 kg
One Mole of SO_2F_2	0.102 06 kg
Specific Volume @ 21.1 °C, 101.325 kPa	231.0 dm^3/kg; 3.7 ft^3/lb
Vapor Pressure @ 21.1 °C	1598 kPa; 15.98 bar; 231.7 psia; 15.77 atm
Boiling Point @ 101.325 kPa	217.77 °K; −55.4 °C; −67.7 °F
Triple Point	137.33 °K; −135.8 °C; −212.5 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	4.486 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	3.72
Density, Liquid @ −80 °C	1.786 kg/l
Critical Temperature	365.0 °K; 91.8 °C; 197.3 °F
Critical Pressure	5117 kPa; 51.17 bar; 742.1 psia; 50.5 atm
Critical Volume	1.636 dm^3/kg
Critical Density	0.611 kg/dm^3
Critical Compressibility Factor	0.282
Latent Heat of Fusion @ 137.33 °K	4.494 kJ/mol; 1.074 kcal/mol
Dipole Moment, Gas	3.703×10^{-30} C·m; 1.110 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	68.643 J/(mol·°K)
Solubility In Water @ 101.325 kPa @ 0 °C	0.016 kg/0.1 kg water
Trouton Constant	22.0

Description

At room temperature and atmospheric pressure, sulfuryl fluoride is a colorless, odorless, nonflammable, noncorrosive, toxic gas. It is shipped in steel cylinders as a liquefied gas under its own vapor pressure of 1 496 kPa (217 psig) at 21.1 °C.

Specifications

Sulfuryl fluoride has a minimum purity of 99.5%.

Uses

Sulfuryl fluoride is used primarily as an insecticidal fumigant, in the preparation of fluorocarbon compounds, and as a catalyst. The Dow Chemical Company owns patents covering the use of this gas as a fumigant, specifically as an agent for the extermination of termites.

Prospective users should refer to Dow for further information for use of sulfuryl fluoride as an insecticide.

Effects in Man and Toxicity (2)

Studies to determine the toxicity of sulfuryl fluoride when inhaled repeatedly (up to 7 hours per day, 5 days per week, for up to 1 year) have been conducted on several animal species. The results of these studies have led to the conclusion that concentrations of gas in work areas where prolonged and repeated exposure is possible should not exceed 10 ppm, and the time-weighted average for 7–8 hour daily exposures should not exceed 5 ppm.

A 30 year male who breathed sulfuryl fluoride for approximately 4 hours under conditions of limited ventilation noted the onset of nausea, vomiting, crampy abdominal pain, and pruritis and left the area. Examination revealed normal vital signs, reddened conjunctivae, pharyngeal and nasal mucosa, diffuse rhonchi, and paresthesia (to pin prick) of the lateral border of the right leg.

Sulfuryl fluoride is practically odorless and thus does not give adequate warning of the presence of excessive concentrations.

The 1979 ACGIH has established a Threshold Limit Value (TLV) of 5 ppm (20 mg/m^3) for sulfuryl fluoride.

First Aid Treatment (2)

There is no specific treatment for this intoxication. The victim should be removed to an uncontaminated atmosphere, placed face downward with head slightly below level of lungs. Keep the victim warm. If breathing stops, give artificial respiration.

NOTE TO PHYSICIAN: First symptoms expected are those of respiratory and central nervous system depression. Treat supportively and symptomatically.

Precautions in Handling and Storage

Sulfuryl fluoride should be used only in a well-ventilated area, preferably a hood with forced ventilation. Appropriate gas masks or self-contained breathing equipment should be kept readily available in areas not likely to become contaminated, for use in emergencies.

In addition, the general rules listed in Appendix I should be observed.

Matheson

Leak Detection

Leaks of sulfuryl fluoride may be detected applying soap water solution to the suspected points; leaks will be indicated by bubble formation.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-C.

Materials of Construction

Since sulfuryl fluoride is noncorrosive, any common metal may be used with this gas at room temperature and atmospheric pressure. At elevated temperatures, some metals will react with sulfuryl fluoride.

Cylinder and Valve Description

Sulfuryl fluoride is shipped in steel cylinders, which comply with DOT specifications.

Cylinders of sulfuryl fluoride are equipped with Compressed Gas Association (CGA) valve outlet No. 660. This outlet has a thread size of 1.030 inches diameter and is right-hand with external threads. The mating connection seats on a flat washer. Figure 1 illustrates the valve outlet and mating connection used in this service.

Lecture bottles have a special outlet designated as 5/16″-32 threads per inch, female.

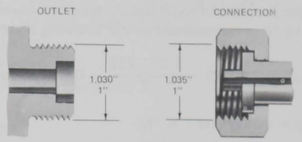


Fig. 1. CONNECTION 660 1.030″-14 RH EXT. using Flat Seat with Washer

Safety Devices

Cylinders containing sulfuryl fluoride have fusible metal plugs, melting at approximately 73.9 °C (165 °F) as a safety device.

Recommended Controls

Automatic Pressure Regulators

Single Stage Regulators

The following Matheson regulators are recommended for use with sulfuryl fluoride.

Model No.	Delivery Pressure Range		
	kPa	bar (g)	psig
1P-660	28–240	0.28–2.4	4–35
1L-660	28–550	0.28–5.5	4–80
1H-660	69–1 240	0.69–12.4	10.180

Regulator No. 3321, with a delivery pressure range of 28–410 kPa (4–60 psig), is available for use with lecture bottles.

Manual Controls

Matheson needle valve Model 50-660 of brass bar stock is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets (¼″ tube fitting, or ¼″ NPT male or female pipe or a hose connection).

A manual valve should be used only where manual control is needed and should not be used as a pressure control, since it will not prevent pressure from building up, if a system becomes clogged or if the system itself is closed. Needle valve Model 31B is recommended for use with the lecture bottles.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Sulfuryl fluoride is classified by the DOT as a nonflammable compressed gas and is shipped with the required "Green Label."

Chemical Preparation

Several methods are available for the preparation of sulfuryl fluoride, some of which are as follows:

1. By passing a mixture of sulfur dioxide and helium or nitrogen over silver (II) fluoride.
2. By pyrolysis of barium fluosulfate at 500–800 °C.
3. By pyrolysis of thionyl tetrafluoride at 450–1 500 °C and 50–4 000 atm to give a mixture of sulfuryl fluoride and sulfur hexafluoride, which is separated by fractionation.
4. By refluxing arsenic trifluoride and sulfur trioxide to give pyrosulfuryl fluoride and arsenic fluosulfate. Pyrolysis of the former at 200–700 °C gives sulfuryl fluoride; pyrolysis of the latter at 700 °C also gives sulfuryl fluoride.
5. By direct interaction of sulfur dioxide and fluorine.

Chemical Properties

Sulfuryl fluoride is thermally very stable, but it attacks glass at 600 °C. Sulfuryl fluoride is inert to water even in a sealed

Matheson

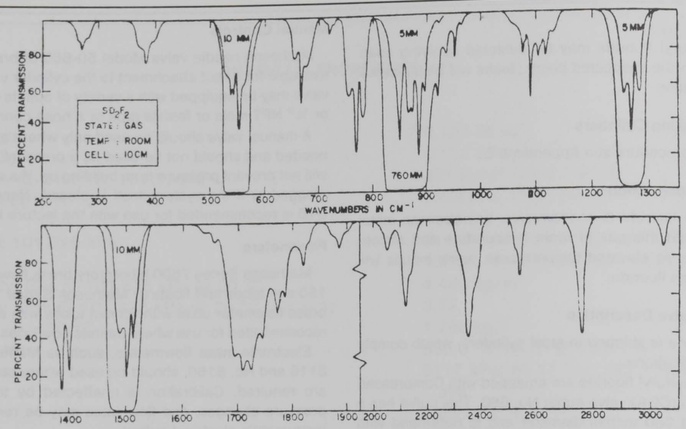


Fig. 2. Infrared spectrum of gaseous sulfuryl fluoride between 250 cm^{-1} and 4 000 cm^{-1}; spectra were obtained with a Perkin-Elmer model 21 spectrophotometer equipped with NaCl and CsBr prisms; 10-cm path length cells with NaCl, KBr or CsBr windows; cell pressures are indicated on the curve (5).

tube at 150 °C. Metals react with sulfuryl fluoride at elevated temperatures; nonmetals are generally inactive toward sulfuryl fluoride, but sulfuryl fluoride with sulfur or selenium will etch glass at 400 °C. Hydrogen sulfide or hydrogen reacts with sulfuryl fluoride at red heat yielding sulfur, water, and hydrogen fluoride. Sulfuryl fluoride is absorbed and hydrolyzed by aqueous solutions of strong bases, such as sodium or potassium hydroxide.

Thermodynamic and Detailed Physical Data

Molecular Structure

Sulfuryl fluoride has C_{2v} point group symmetry and a symmetry number of two, with the following structural parameters: bond distances: S═O 1.405 Å (1.405 × 10^{-10} m); S—F 1.530 Å (1.530 × 10^{-10} m); bond angles: O—S—O 123.97°; F—S—F 96.12°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous sulfuryl fluoride.

Vapor Pressure

The vapor pressure of liquid sulfuryl fluoride between 163.15 and 223.15 °K is represented by the following equation (3):

$$\log_{10}p = 7.832\,3 - \frac{1\,071.235}{T} - 0.013\,91 \log_{10}T$$

in which p = mmHg and T = °K.

Latent Heat of Vaporization (3) @ 217.77 °K	19.230 kJ/mol; 4.569 kcal/mol

Thermodynamic Properties of Sulfuryl Fluoride As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	68.434 J/(mol·°K)
Entropy, S°	288.206 J/(mol·°K)
Free Energy Function, $(F^\circ_{298} - H^\circ_{298})/298$	−288.206 J/(mol·°K)
Enthalpy Difference, $H^\circ_{298} - H^\circ_0$	14.251 kJ/mol
Enthalpy of Formation, ΔH_f°	−857.720 kJ/mol
Free Energy of Formation, ΔF_f°	−812.562 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of sulfuryl fluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 144-146, Matheson, Lyndhurst, New Jersey.

[3] F. J. Bockhoff, R. V. Petrella, and E. L. Pace, *J. Chem. Phys.* 32, 799-804, (1960).

[4] **JANAF Thermochemical Tables**, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[5] G. R. Hunt and M. K. Wilson, *Spectrochim. Acta* 16, 570-574 (1960).

TETRAFLUOROETHYLENE

(Formula: $F_2C{:}CF_2$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.100 016 kg
One Mole of $F_2C{:}CF_2$	0.100 016 kg
Specific Volume @ 21.1 °C, 101.325 kPa	237.2 dm^3/kg; 3.8 ft^3/lb
Vapor Pressure @ 21.1 °C	3 040 kPa; 30.4 bar; 441.3 psia; 30.0 atm
Boiling Point @ 101.325 kPa	196.85 °K; −76.3 °C; −105.3 °F
Freezing Point	−130.65 °K; −142.5 °C; −224.5 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	4.255 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	3.53
Density, Liquid @ −20 °C	1.30 kg/l
Critical Temperature	306.45 °K; 33.3 °C; 91.9 °F
Critical Pressure	3 944 kPa; 39.44 bar; 572.0 psia; 38.92 atm
Critical Volume	1.720 dm^3/kg
Critical Density	0.581 kg/dm^3
Critical Compressibility Factor	0.266
Flammability Limits In Air	14-43% (by volume)
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	80.458 J/(mol·°K)
Solubility In Water @ 101.325 kPa @ 30 °C	0.01 kg/100 kg of water
Dielectric Constant, Gas @ 28 °C	
@ 103 kPa	1.001 7
@ 862 kPa	1.015
Autoignition Temperature	893.15 °K; 620 °C; 1 148 °F

Description

Tetrafluoroethylene is a colorless, flammable, nontoxic gas at room temperature and atmospheric pressure. It is very reactive and is capable of polymerization with explosive violence. It must be stabilized with an inhibitor, usually 1% by weight of α-terpinene or α-pinene for transportation. It is shipped in steel cylinders as a compressed gas at 1 034 kPa (150 psig) at 21.1 °C.

Specifications

Commercial tetrafluoroethylene usually has a minimum purity of 99.0%.

Uses

Tetrafluoroethylene is used primarily for the synthesis of polymers and copolymers.

Toxicity

Tetrafluoroethylene does not appear to have any substantial toxicity, but is should nevertheless be used in a well-ventilated area, preferably a hood with forced ventilation.

Precautions in Handling and Storage

The monomeric tetrafluoroethylene can autopolymerize rapidly under the effects of temperature and pressure, especially if a catalyst such as oxygen is present. All efforts to eliminate the presence of oxygen should be taken to prevent self-polymerization.

For some chemical reactions it is possible to use the tetrafluoroethylene directly from the cylinder by using the vapor phase, thereby effecting a one-step distillation. This should effectively remove a major portion of the inhibitor. Polymerization of the tetrafluoroethylene can only take place if the inhibitor is completely removed. This can be effected only by distillation in a column with at least the equivalent of four plates.

Store and use tetrafluoroethylene cylinders in well-ventilated areas away from heat and all sources of ignition such as flames and sparks. Never use flames to detect flammable gas leaks, use soapy water. Do not use tetrafluoroethylene around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of tetrafluoroethylene with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials. Ground all lines used with tetrafluoroethylene.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks of tetrafluoroethylene in lines or equipment may be detected by painting the suspected sites with soap water. Leaks will be indicated by bubble formation. Never use a flame to detect leaks.

Disposal of Leaking Cylinders

Leaking cylinders of tetrafluoroethylene may be disposed of according to the procedure described in Appendix II-A. Alternatively, the gas may be introduced into a concentrated aqueous solution of sodium bisulfite or into a 10% alcoholic solution of sodium methoxide or sodium hydroxide.

Materials of Construction

Since tetrafluoroethylene is a noncorrosive gas, any common or commercially available metal may be used. However, piping systems or vessels to contain tetrafluoroethylene should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

Tetrafluoroethylene is shipped in DOT approved steel cylinders. The cylinder is equipped with valves having Compressed Gas Association (CGA) valve outlet No. 350 which has a thread size of 0.825 inch diameter, left-hand external threads, accepting a round shaped nipple (see Figure 1).

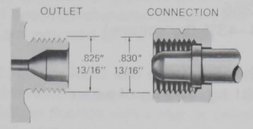


Fig. 1. CONNECTION 350 .825″-14 LH EXT. accepting Round Shaped Nipple

Safety Devices

Cylinders of tetrafluoroethylene have frangible discs as safety devices. Cylinders should, therefore, be stored away from sources of heat to avoid developing pressures capable of rupturing the disc.

Recommended Controls

Automatic Pressure Regulators

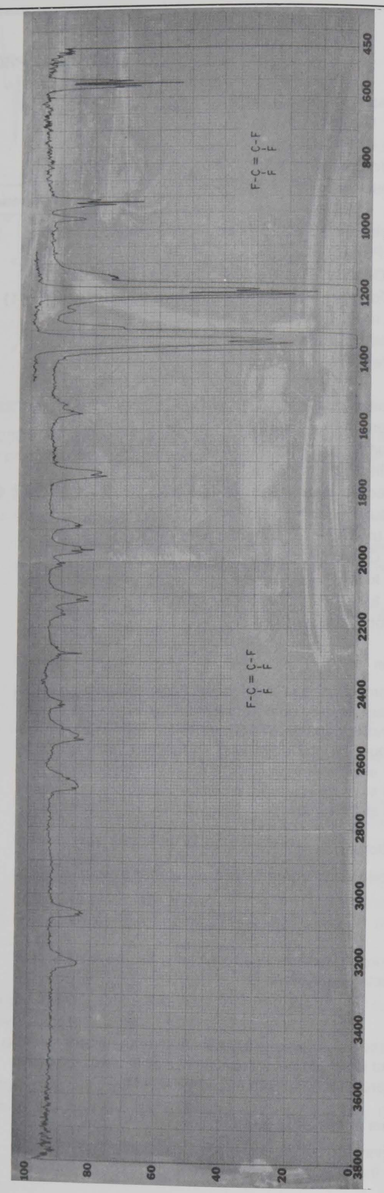
Matheson supplies single stage metal diaphragm regulator Model 19-350 for use with tetrafluoroethylene. The regulator has a brass body, German silver diaphragm, nylon seat, aluminum and nylon gaskets, and a diaphragm packless outlet valve with ¼″ Gyrolok tube fitting. It has a delivery pressure range of 28–345 kPa (4–50 psig).

Manual Controls

Diaphragm packless valve Model 4351-350 is available for direct attachment to the cylinder valve outlet. This type of control is mainly used for control of intermittent flows or where it is desired to control the flow of gas directly from the cylinder. However, pressure cannot be controlled with such a valve, and if a line or system becomes plugged, dangerous pressures can build up.

Flowmeters

Matheson Series 7600 laboratory brass flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory



Reprinted through the courtesy of Sadtler Research Laboratories

©Sadtler 1972

Fig. 2. Infrared spectrum of gaseous tetrafluoroethylene; 10-cm path length cell; cell pressure: curve A (complete scan): 2.666 kPa (20 mmHg); curve B (partial scan): 0.066 7 kPa (0.5 mmHg) (6).

brass flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes. Flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Tetrafluoroethylene is shipped in high pressure steel cylinders as a flammable compressed gas, requiring a DOT "Red Gas Label".

Commercial Preparation

Tetrafluoroethylene is prepared commercially by pyrolysis of chloro- or bromodifluoromethane, at 600–800 °C. In the laboratory, it is readily prepared by dehalogenation of symmetrical dihalotetrafluoroethanes by metals at temperatures above 100 °C or by depolymerization of polytetrafluoroethylene at about 600 °C at reduced pressure.

Chemical Properties (1) (3)

Tetrafluoroethylene is absorbed by 47% fuming sulfuric acid, but it is not affected by the concentrated acid. Aqueous acids or bases are without effect except at very high temperatures. Chlorine and bromine add readily. Iodine in aqueous potassium iodide solution does not react, but at elevated pressures of the olefin it adds. In aqueous solution, tetrafluoroethylene adds sodium bisulfite to form 1,1,2,2-tetrafluoroethanesulfonic acid sodium salt; this is also accompanied by some hydrolysis to difluoroacetic acid sodium salt. Alkali alcoholates or hydroxides in ethanol solution add the elements ROH to form 1,1,2,2-tetrafluoroethyl alkyl ethers. Phenols are reported to react as well as the alcohols.

Tetrafluoroethylene adds primary aliphatic amines under similar conditions. In aqueous base, addition and hydrolysis occurs according to the reaction:

$$CF_2{:}CF_2 + RNH_2 + 2OH^- \rightarrow CF_2HCONHR + 2F^- + H_2O.$$

Secondary amines give N,N-disubstituted amides. Ammonia reacts somewhat differently to form the trimer 2,4,6-tris-(difluoromethyl)-1,3,5-triazine. Tetrafluoroethylene polymerizes readily under pressure. The purified oxygen-free gas is relatively stable, but traces of oxygen, bases, peroxides, and amine oxides are polymerization catalysts while antioxidants such as amines and thiols are effective retardants.

Tetrafluoroethylene dimerizes to form octafluorocyclobutane, slowly at room temperature and rapidly at about 500 °C; it reacts with nonfluorinated olefins to form the corresponding cyclobutane derivative. On heating at 600–700 °C, tetrafluoroethylene undergoes a series of exothermic reactions, in which octafluorocyclobutane, hexafluoropropylene, and octafluoroisobutylene are formed successively with increasing contact time at constant temperature.

Thermodynamic and Detailed Physical Data

Molecular Structure (4)

Tetrafluoroethylene is a planar molecule, with D_{2h} point group symmetry and a symmetry number of four, with the following bond distances and angles: C—F 1.313 Å (1.313×10^{-10} m); C—C 1.313 Å (1.313×10^{-10} m); F—C—F 114°.

Infrared Spectrum (6)

See Figure 2 for the infrared spectrum of gaseous tetrafluoroethylene.

Vapor Pressure (5)

The vapor pressure of liquid tetrafluoroethylene between 196.85 and 273.15 °K is represented by the following equation:

$$\log_{10} p = 5.621\ 0 - 875.14/T$$

in which p = lbf/in² absolute (psia) and T = °K. Between 273.15 and 306.35 °K, the vapor pressure is represented by the following equation:

$$\log_{10} p = 5.590\ 6 - 866.84/T$$

in which p = psia and T = °K.

Thermodynamic Properties of Tetrafluoroethylene As Ideal Gas @ 25 °C (4)

Heat Capacity, C_p°	80.458 J/(mol·°K)
Entropy, S°	299.901 J/(mol·°K)
Free Energy Function, $(F^\circ_{298} - H^\circ_{298})/298$	−299.901 J/(mol·°K)
Enthalpy Difference, $H^\circ_{298} - H^\circ_0$	16.330 kJ/mol
Enthalpy of Formation, ΔH_f°	−658.562 kJ/mol
Gibbs Energy of Formation, ΔG_f°	−623.717 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of tetrafluoroethylene, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] *Fluorine Chemistry*, J. H. Simons, editor, *1950*, Volume 1, pp. 473–474, Academic Press Inc., New York, New York.
[3] S. Sherratt in Kirk-Othmer's **Encyclopedia of Chemical Technology**, *1966*, Volume 9, p. 810, John Wiley & Sons, Inc., New York, New York.
[4] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.
[5] M. M. Renfrew and E. E. Lewis, *Ind. Eng. Chem.* 38, 870 (1948).
[6] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

TETRAFLUOROHYDRAZINE

(Synonym: Dinitrogen Tetrafluoride)
(Formula: N_2F_4)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.104 007 kg
One Mole of N_2F_4	0.104 007 kg
Specific Volume @ 21.1 °C, 101.325 kPa	232.2 dm^3/kg; 3.72 ft^3/lb
Cylinder Pressure @ 21.1 °C	791 kPa; 7.91 bar; 114.7 psia; 7.80 atm
Absolute Density, Gas @ 101.325 kPa @ 20 °C	4.405 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	3.66
Density, Liquid @ 173.15 °K	1.5 kg/l
Boiling Point @ 101.325 kPa	200.15 °K; −73.0 °C; −99.4 °F
Melting Point	105.15 °K; −168.0 °C; −270.4 °F
Critical Temperature	309.15 °K; 36.0 °C; 96.8 °F
Critical Pressure	7 800 kPa; 78.0 bar; 1 131.6 psia; 77 atm
Critical Volume	0.931 dm^3/kg
Critical Density	1.074 kg/dm^3
Critical Compressibility Factor	0.294
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	79.200 J/(mol·°K)

Description

Tetrafluorohydrazine is a colorless, toxic gas with a characteristic musty odor. It is shipped as a nonliquefied gas in small cylinders and lecture bottles at cylinder pressures of 690 kPa (100 psig) and 170 kPa (25 psig), respectively, at 21.1 °C.

Specifications

Tetrafluorohydrazine is supplied in small cylinders in a Research Grade, C.P. Grade, and Technical Grade with purities of 99.8, 99.0, and 98.0%, respectively.

Uses

Tetrafluorohydrazine is of interest as an oxidizer of high energy fuels and as a reactant in both inorganic and organic synthesis.

Toxicity

The 1979 ACGIH has not set a Threshold Limit Value (TLV) for this gas. It is slowly hydrolyzed by water and the resulting hydrolytic products, hydrazine and hydrogen fluoride, are quite toxic. Tetrafluorohydrazine should be regarded as a highly toxic gas and handled accordingly.

First Aid Treatment

It is suggested that the first aid treatment described for exposure to hydrogen fluoride be followed.

Precautions in Handling and Storage

Tetrafluorohydrazine should be handled in a hood with forced ventilation and, preferably, behind a barricade until the danger of explosion of a particular reaction has been fully investigated. Heat, shock, or blast can detonate it when under pressure.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks of tetrafluorohydrazine in lines and equipment may be detected by applying soap water solution to the suspected sites. Leaks will be indicated by bubble formation.

Materials of Construction

Tetrafluorohydrazine may be handled in glass, stainless steel, copper, or nickel at temperatures up to 200 °C. Only nickel and monel are recommended for higher temperatures.

Cylinder and Valve Description

Tetrafluorohydrazine is shipped in DOT approved steel cylinders. The cylinders have brass valves with Compressed Gas Association (CGA) valve outlet connection No. 679. The valve outlet has a thread size of 1.030 inch, with left-hand external threads using a small flat seat with washers (see Figure 1 for details).

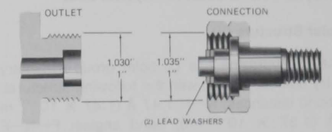


Fig. 1. CONNECTION 679 1.030"-14 LH EXT. using Small Flat Seat with Washer

Recommended Controls

Manual Controls

Matheson needle valve Model 55-679 is available for direct attachment to the cylinder valve outlet. These needle valves are of monel stock, and may be equipped with a variety of outlets (¼" tube fitting or ¼" NPT male or female pipe or a hose connection). Matheson Model 60L monel needle valve is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory monel flowmeter units with 150 mm tubes and floats are recommended for use where definite flow rates must be known.

Electronic Mass Flow Controllers

The Matheson Series 8260 of monel is designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Tetrafluorohydrazine is classfied by the DOT as "Compressed Gases, n.o.s." and takes a DOT label: "Flammable Gas".

Chemical Preparation

Tetrafluorohydrazine is prepared by reaction of nitrogen fluoride with metals at elevated temperatures. It is also obtained in low yield from the reaction between fluorine and ammonia, or by removal of hydrogen from difluoroamine.

Chemical Properties

Tetrafluorohydrazine is hydrolyzed slowly by water. It dissociates into nitrogen and nitrogen trifluoride when heated with a hot wire, but when heated from room temperature at 1 atmosphere pressure to 300 °C, it dissociates into nitrogen difluoride radicals to the extent of 90%. It reacts with diborane to give a mixture of fluoroborazines. It reacts with alkyl iodides to give compounds such as CH_3NF_2.

Thermodynamic and Detailed Physical Data

Molecular Structure (2)

Tetrafluorohydrazine has C_2 point group symmetry and a symmetry number of two, with the following structural parameters: bond distances: N—N 1.47 Å (1.47 × 10^{-10} m); N—F 1.37 Å (1.37 × 10^{-10} m); bond angles: F—N—F 108°; N—N—F 104°; dihedral angle 65°.

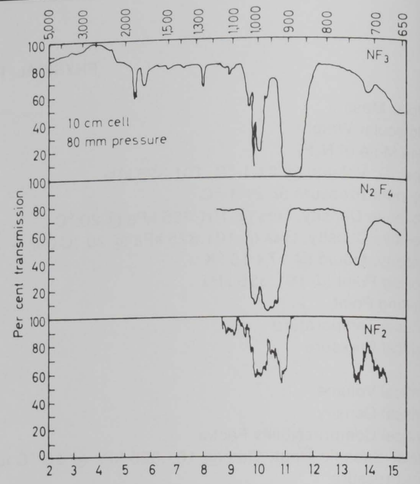


Fig. 2. Infrared spectrum of gaseous tetrafluorohydrazine along with NF_3 and NF_2 for comparison; 10-cm cell; cell pressure: 10.666 kPa (80 mmHg) (4).

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous tetrafluorohydrazine.

Vapor Pressure (3)

The vapor pressure of liquid tetrafluorohydrazine is represented by the following equation:

$$\log_{10} p = 6.33 - 692/T$$

in which p = mmHg and T = °K.

Latent Heat of Vaporization (3) @ 200.15 °K	13.263 kJ/mol; 3 170 cal/mol

Thermodynamic Properties of Tetrafluorohydrazine As Ideal Gas @ 25 °C (2)

Heat Capacity, C_p°	79.170 J/(mol·°K)
Entropy, S°	301.089 J/(mol·°K)
Free Energy Function, $(F^\circ_{298} - H^\circ_{298})/298$	−301.089 J/(mol·°K)
Enthalpy Difference, $H^\circ_{298} - H^\circ_0$	15.523 kJ/mol
Enthalpy of Formation, ΔH_f°	−8.368 kJ/mol
Free Energy of Formation, ΔF_f°	79.831 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of tetrafluorohydrazine, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[3] C. B. Colburn and A. Kennedy, *J. Amer. Chem. Soc.* 80, 5004 (1958).

[4] C. B. Colburn in **Adv. Fluor. Chem.**, M. Stacey, J. C. Tatlow, and A. G. Sharpe, editors, *1963*, Volume 3, p. 112, Butterworth, Inc., Washington, D. C.

TRICHLOROFLUOROMETHANE

(Synonym: Freon-11®)
(Formula: CCl_3F)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.137 368 kg
One Mole of CCl_3F	0.137 368 kg
Vapor Pressure @ 21.1 °C	92 kPa; 0.92 bar; 13.4 psia; 0.91 atm
Boiling Point @ 101.325 kPa	296.97 °K; 23.8 °C; 74.9 °F
Freezing Point	162.04 °K; −111.1 °C; −168.0 °F
Absolute Density, Saturated Vapor @ 23.8 °C	5.85 kg/m^3
Density, Liquid @ 25 °C	1.476 kg/l
Critical Temperature	471.15 °K; 198.0 °C; 388.4 °F
Critical Pressure	4 408 kPa; 44.08 bar; 639.3 psia; 43.5 atm
Critical Volume	1.806 dm^3/kg
Critical Density	0.554 kg/dm^3
Critical Compressibility Factor	0.279
Latent Heat of Fusion @ 162.04 °K	50.208 kJ/kg; 6.897 kJ/mol
Dipole Moment, Gas	1.534×10^{-30} C·m; 0.46 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C	77.613 J/(mol·°K); 0.135 kcal/(kg·°K)
@ Constant Pressure	
@ Constant Volume	68.321 J/(mol·°K); 0.119 kcal/(kg·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.136
Molar Specific Heat, Liquid @ 287.81 °K	120.403 J/(mol·°K); 28.777 cal/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 297.04 °K	0.010 5 mPa·s; 0.010 5 cP
Viscosity, Liquid @ 20 °C	0.43 mPa·s; 0.43 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 297.04 °K	0.007 57 W/(m·°K); 18.1×10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ 277.59 °K	0.093 4 W/(m·°K); 223.2×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 277.59 °K	21.0 mN/m; 21.0 dyn/cm
Solubility In Water @ Saturation Pressure @ 277.59 °K	0.145 weight %
Refractive Index, n_D	
Liquid @ 21.1 °C	1.379 9
Saturated Vapor @ 21.1 °C	1.001 25
Dielectric Constant Liquid @ 21.1 °C	2.30
Vapor @ 21.1 °C, 50.7 kPa	1.002 6
Relative Dielectric Strength (Nitrogen = 1)	3.71

Description

Trichlorofluoromethane is a water-white nonflammable volatile liquid. In concentrations of less than 20% (by volume in air), trichlorofluoromethane is odorless; in higher concentrations, its odor is mild and somewhat ethereal. Trichlorofluoromethane is relatively nontoxic. It is shipped as a liquid in drum and cans and ton containers under its own vapor pressure of 92.4 kPa (13.4 psia) at 21.1 °C.

Specifications

Trichlorofluoromethane has a minimum purity of 99.9 mole %.

Uses

Trichlorofluoromethane is used as a refrigerant, as a heat transfer medium, as a solvent, as a propellant (mixed with other

Freon compounds) in insecticidal aerosols and as a chemical intermediate.

Effects In Man and Toxicity (2)

Inhalation of high concentrations of gas can cause such symptoms as dizziness, disorientation, incoordination, narcosis, nausea, or vomiting. There appear to be no irreversible effects once the oxygen deficiency has been corrected.

First Aid Treatment (2)

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration and oxygen simultaneously. Treat symptomatically thereafter.

Precautions in Handling and Storage

The following rules should be followed in the handling and storage of trichlorofluoromethane.

Since trichlorofluoromethane is relatively nontoxic and a nonflammable liquid of low vapor pressure, the usual precautions associated with the handling of compressed gases are not applicable. However, the material should be handled in a well-ventilated area, and contact with flames or high heat should be avoided, since decomposition can take place with the formation of toxic halogen by-products.

Leak Detection

A more sensitive means of leak detection is provided by the Matheson Gas Leak Detector Models 8016 and 8017.

Materials of Construction

Most of the commonly used metals (steel, cast iron, brass, copper, tin, lead, aluminum) may be used satisfactorily with trichlorofluoromethane under normal conditions of use and especially in a dry system. At high temperatures some of the metals may act as catalysts for the breakdown of the compound. The tendency of metals to promote thermal decomposition of trichlorofluoromethane is in the following approximate order: silver > brass > bronze > aluminum > 1340 steel > copper > nickel > 18-8 stainless steel > inconel (least decomposition). Magnesium alloys and aluminum containing more than 2% magnesium are not recommended for use in systems containing trichlorofluoromethane where water may be present.

In general, gasket materials should not contain natural rubber. Neoprene or Isoprene rubber, pressed fibers, including asbestos, with a number of insoluble binders, and metallic gaskets may be used.

Cylinder and Valve Description

Trichlorofluoromethane is packaged in DOT approved drums. Drums have a ¾ inch I.P.S. female outlet.

Recommended Controls

Because of the low pressure, it is recommended that the drum be used either with an ordinary globe or gate valve, or drum spigot valve.

Shipping Regulations

Trichlorofluoromethane is shipped as a nonflammable chemical. It does not require DOT shipping labels.

Commercial Preparation

Trichlorofluoromethane is prepared by fluorinating carbon tetrachloride with anhydrous hydrogen fluoride at elevated temperatures under pressure.

Chemical Properties

Trichlorofluoromethane is thermally stable, only 2% decomposition per year occurring on heating trichlorofluoromethane to 200 °C (392 °F) in steel. Trichlorofluoromethane is nonflammable in any mixture with air and will not explode or propagate a flame. The rate of hydrolysis of trichlorofluoromethane in water in steel is only 0.028 kg/l year. Trichlorofluoromethane is noncorrosive to steel, cast iron, brass, copper, tin, lead, and aluminum under normal conditions. At elevated temperatures, corrosion does occur. Trichlorofluoromethane undergoes further fluorination with hydrogen fluoride in the presence of catalysts. Trichlorofluoromethane under the influence of aluminum bromide or aluminum chloride disproportionates to carbon tetrachloride, dichlorodifluoromethane, and chlorotrifluoromethane.

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

Trichlorofluoromethane has C_{3v} point group symmetry and a symmetry number of three. The structural parameters are the following: bond distances: C—Cl 1.76 Å (1.76×10^{-10} m); C—F 1.33 Å (1.33×10^{-10} m); bond angles: Cl—C—Cl 109.67°; F—C—Cl 109.47°.

Infrared Spectrum

See Figure 1 for the infrared spectrum of gaseous trichlorofluoromethane.

Vapor Pressure (4)

The vapor pressure of liquid CCl_3F between 0.276 and 4 495 kPa is represented by the following equation:

$$\log_{10} p = A + \frac{B}{T} + C \log_{10} T + DT + \frac{E(F - T)}{T} \log_{10}(F - T)$$

in which p = lbf/in^2 absolute (psia) and T = °R (= °F + 459.67), and the constants have the following values:

A = 42.147 028 65	D = 0.004 008 372 507
B = −4 344.343 807	E = 0.031 360 535 6
C = −12.845 967 53	F = 862.07

For specific vapor pressure data, see Table 1 and Figure 2.

Latent Heat of Vaporization, ΔHv @ 296.97 °K	182.05 kJ/kg; 43.51 kcal/kg; 78.31 Btu/lb

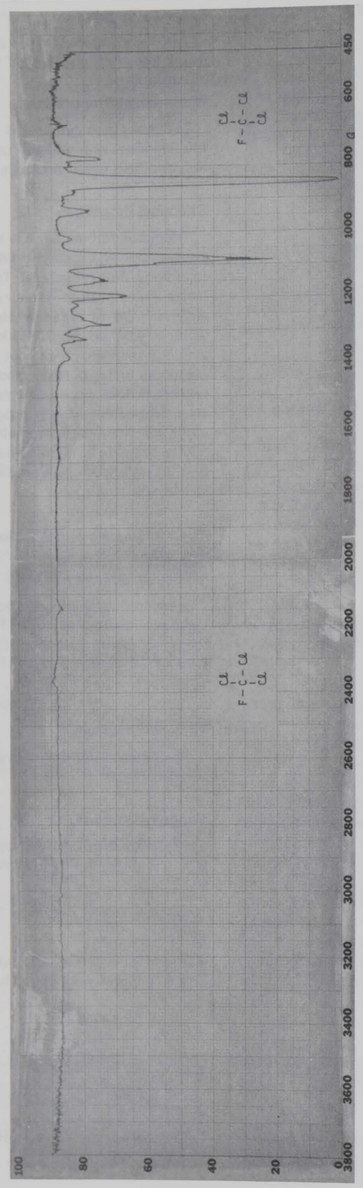


Fig. 1. Infrared spectrum of gaseous trichlorofluoromethane; 10-cm path length cell, with KBr windows; cell pressure: 6.667 kPa (50 mmHg) (5).

Thermodynamic Data

Thermodynamic properties for the saturated liquid and vapor and for the superheated vapor are listed in Tables 1 and 2, respectively.

Thermodynamic Properties of Trichlorofluoromethane As Ideal Gas @ 25 °C (3)

Heat Capacity, C_p°	78.015 J/(mol·°K)
Entropy, S°	309.624 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−309.620 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	16.058 kJ/mol
Enthalpy of Formation, ΔH_f°	−288.696 kJ/mol
Free Energy of Formation, ΔF_f°	−249.383 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of trichlorofluoromethane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 119–123, Matheson, Lyndhurst, New Jersey.

[3] *JANAF Thermochemical Tables*, 2nd edition, *1971*, D. R. Stull and H. Prophet, project directors, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C.

[4] *Thermodynamic Properties of Freon-11*, Tech. Bull. T-11, *1965*, E. I. duPont de Nemours and Co., Wilmington, Delaware.

[5] *The Sadtler Standard Spectra*, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED TRICHLOROFLUOROMETHANE (4)

Temperature °K		Pressure		Entropy J/(mol·°K)		Enthalpy J/mol		Latent Heat of Vaporization kJ/mol	Specific Volume dm^3/kg		Density kg/dm^3	
°K	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
166.48	−160	0.010 84	0.000 107	−39.396	149.182	−7 793	23 602	31 395	0.568 2	926.199	1.760 0	0.000 001
177.59	−140	0.044 38	0.000 438	−31.750	141.325	−6 478	24 259	30 737	0.575 5	242 277	1.737 6	0.000 004
188.71	−120	0.149 5	0.001 48	−24.612	134.945	−5 172	24 938	30 110	0.583 0	76 418	1.715 3	0.000 013
199.82	−100	0.430 3	0.004 25	−17.923	129.761	−3 873	25 638	29 511	0.590 9	28 085	1.692 3	0.000 036
210.93	−80	1.089	0.010 74	−11.623	125.559	−2 579	26 357	28 936	0.599 0	11 710	1 669 4	0.000 083
222.04	−60	2.472	0.024 4	−5.664	122.157	−1 289	27 092	28 381	0.607 5	5 422	1.646 1	0.000 184
233.15	−40	5.124	0.050 6	0.000	119.410	0.000	27 841	27 841	0.616 4	2 742	1.622 3	0.000 365
244.26	−20	9.831	0.097 0	5.407	117.208	1 291	28 600	27 309	0.625 6	1 493	1.598 5	0.000 670
255.37	0	17.655	0.174 2	10.587	115.455	2 586	29 366	26 780	0.635 3	865.6	1.574 1	0.001 16
266.48	20	29.955	0.295 6	15.568	114.076	3 886	30 137	26 251	0.645 4	529.5	1.549 4	0.001 89
277.59	40	48.417	0.477 8	20.367	112.995	5 193	30 907	25 714	0.656 1	339.0	1.524 2	0.002 95
288.71	60	74.987	0.740 1	25.004	112.174	6 508	31 674	25 166	0.667 4	255.7	1.498 4	0.004 43
299.82	80	111.923	1.105	29.490	111.553	7 832	32 436	24 604	0.679 3	155.4	1.472 1	0.006 44
310.93	100	161.723	1.596	33.838	111.104	9 164	33 188	24 024	0.692 0	110.2	1.445 1	0.009 07
322.04	120	227.134	2.242	38.062	110.794	10 507	33 929	23 422	0.705 6	80.06	1.417 2	0.012 49
333.15	140	311.112	3.070	42.172	110.593	11 861	34 656	22 795	0.720 2	59.45	1.388 5	0.016 82
344.26	160	416.795	4.113	46.182	110.478	13 230	35 365	22 135	0.735 8	44.97	1.359 1	0.022 04
355.37	180	547.540	5.404	50.105	110.426	14 616	36 052	21 436	0.752 9	34.56	1.328 2	0.028 94
366.48	200	706.850	6.976	53.960	110.421	16 024	36 715	20 691	0.771 6	26.91	1.296 0	0.037 16
377.59	220	898.456	8.867	57.762	110.438	17 460	37 348	19 888	0.792 3	21.19	1.262 1	0.047 19
388.71	240	1 126.26	11.115	61.538	110.449	18 932	37 944	19 012	0.815 4	16.83	1.226 4	0.059 42
399.82	260	1 394.40	13.762	65.314	110.444	20 450	38 494	18 044	0.841 8	13.45	1.187 9	0.074 35
410.93	280	1 707.35	16.850	69.125	110.380	22.031	38 985	16 954	0.872 3	10.78	1.146 4	0.092 76
422.04	300	2 069.87	20.428	73.010	110.219	23 694	39 398	15 704	0.908 8	8.653	1.100 4	0.115 57
433.15	320	2 487.01	24.545	77.039	109.892	25 470	39 701	14 231	0.953 9	6.912	1.048 3	0.144 68
444.26	340	2 964.47	29.257	81.321	109.288	27 413	39 837	12 424	1.013 6	5.546	0.986 6	0.180 31
455.37	360	3 508.33	34.625	86.080	108.127	29.634	39 673	10 039	1.102 1	4.182	0.907 4	0.239 12
466.48	380	4 125.82	40.719	92.167	105.340	32 544	38 687	6 143	1.284 1	2.907	0.778 8	0.340 00
471.15	388.40	4 409.20	43.515	98.966	98.966	35 788	35.788	0	1.805 9	1.805 9	0.553 7	0.553 7

Matheson

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED TRICHLOROFLUOROMETHANE (4)

H, ENTHALPY, J/MOL; S, ENTROPY, J/(MOL·°K); V, SPECIFIC VOLUME, DM^3/KG

Pressure kPa	atm		Temperature, °K 233.15	255.37	277.59	299.82	322.04	344.26	366.48	388.71	410.93	433.15	455.37	477.59	499.82	522.04	544.26	566.48
3.447	0.034	H	27.851	29.433	31.081	32.789	34.551	36.362	38.219	40.116								
(226.95 °K)*		S	122.737	129.215	135.405	141.319	146.986	152.423	157.653	162.677								
		V	4.081	4.474	4.866	5.257	5.648	6.039	6.430	6.821								
13.790	0.136	H		29.385	31.042	32.756	34.524	36.339	38.199	40.100	42.036							
(252.38 °K)*		S		117.565	123.783	129.721	135.411	140.859	146.095	151.130	155.975							
		V		1.111	1.210	1.309	1.408	1.506	1.605	1.703	1.801							
34.474	0.340	H			30.962	32.690	34.469	36.294	38.161	40.066	42.007	43.981						
(269.62 °K)*		S			115.961	121.950	127.674	133.152	117.714	143.457	148.308	152.986						
		V			479.4	519.8	559.9	599.8	639.4	679.0	718.4	757.8						
68.948	0.680	H				32.579	34.377	36.216	38.095	40.010	41.959	43.939	45.947					
(286.49 °K)*		S				115.927	121.709	127.231	132.520	137.946	142.468	147.158	151.682					
		V				256.6	277.2	297.6	317.7	337.8	357.7	377.6	397.4					
101.325	1.000	H				32.471	34.288	36.143	38.033	39.957	41.913	43.899	45.911					
(296.97 °K)*		S				112.467	118.312	123.881	129.198	134.296	139.192	143.894	148.429					
		V				172.4	186.8	201.0	214.9	228.7	242.5	256.1	269.7					
137.895	1.361	H					34.167	36.058	37.962	39.897	41.861	43.854	45.872	47.914				
(306.01 °K)*		S					115.524	121.145	126.502	131.629	136.543	141.261	145.808	150.182				
		V					135.7	146.4	156.8	167.2	177.3	187.5	197.5	207.5				
206.843	2.041	H					33.999	35.896	37.826	39.781	41.762	43.767	45.796	47.847				
(318.89 °K)*		S					111.708	117.432	122.864	128.042	133.002	137.750	142.319	146.716				
		V					88.51	95.95	103.2	110.2	117.2	124.1	130.9	137.6				
275.790	2.722	H						35.728	37.696	39.663	41.661	43.680	45.720	47.779	49.858			
(328.79 °K)*		S						114.685	120.197	125.439	130.433	135.221	139.813	144.227	148.480			
		V						70.70	76.32	81.79	87.12	92.37	97.66	102.7	107.8			
344.738	3.402	H						35.554	37.543	39.543	41.559	43.592	45.642	47.711	49.797			
(336.96 °K)*		S						112.461	118.059	123.358	128.404	133.221	137.836	142.273	146.543			
		V						55.51	60.19	64.69	69.06	73.35	77.57	81.72	85.84			
413.685	4.083	H						35.373	37.396	39.420	41.455	43.502	45.562	47.642	49.736			
(343.97 °K)*		S						110.558	116.254	121.617	126.703	131.554	136.198	142.078	144.940			
		V						45.35	49.41	53.28	57.02	60.66	64.23	67.74	71.22			
482.633	4.763	H							37.244	39.295	41.349	43.411	45.485	47.573	49.674	51.790		
(350.14 °K)*		S							114.668	120.099	125.238	130.123	134.796	139.273	143.572	147.710		
		V							41.70	45.12	48.41	51.59	54.70	57.75	60.76	63.74		
551.581	5.444	H							37.088	39.166	41.241	43.319	45.405	47.503	49.612	51.734		
(355.68 °K)*		S							113.243	118.749	123.939	128.864	133.560	138.054	142.377	146.526		
		V							35.99	38.99	41.94	44.78	47.55	50.26	52.92	55.55		
620.528	6.124	H							36.926	39.035	41.131	43.225	45.325	47.432	49.549	51.678		
(360.73 °K)*		S							111.932	117.519	122.766	127.726	132.456	136.974	141.307	145.474		
		V							31.36	34.21	36.90	39.49	41.99	44.43	46.82	49.19		
689.476	6.805	H							36.758	38.900	41.019	43.130	45.243	47.360	49.486	51.622		
(365.37 °K)*		S							110.714	116.386	121.691	126.692	131.451	135.991	140.342	144.520		
		V							27.72	30.38	32.87	35.24	37.53	39.76	41.94	44.09		
965.266	9.526	H								38.320	40.547	42.735	44.905	47.067	49.228	51.392	53.561	
(381.05 °K)*		S								112.472	118.047	123.231	128.117	132.755	137.175	141.411	145.480	
		V								20.44	22.45	24.30	26.06	27.75	29.38	30.98	32.55	
1 241.06	12.25	H									40.027	42.311	44.548	46.960	51.155	53.349		
(393.68 °K)*		S									115.007	120.415	125.456	130.198	134.704	138.997	143.112	
		V									16.58	18.18	19.66	21.05	22.39	23.69	24.95	
1 378.95	13.61	H									39.744	42.066	44.361	46.602	48.823	51.034	53.241	55.449
(399.22 °K)*		S									114.605	119.951	124.978	129.663	134.029	138.095	142.095	146.072
		V									14.49	16.02	17.40	18.70	19.94	21.13	22.29	23.42
1 654.74	16.33	H									38.117	41.603	43.969	46.272	48.540	50.786	53.021	55.251
(409.17 °K)*		S									110.696	116.789	122.117	127.059	131.698	136.095	140.290	144.302
		V									11.29	12.74	14.01	15.17	16.26	17.30	18.30	19.27
1 930.53	19.05	H										41.067	43.548	45.925	48.245	50.530	52.796	55.050
(417.96 °K)*		S										114.547	120.140	125.232	129.979	134.456	138.704	142.767
		V										10.34	11.55	12.62	13.61	14.55	15.44	16.30

* (Saturation temperatures in parentheses)

Matheson

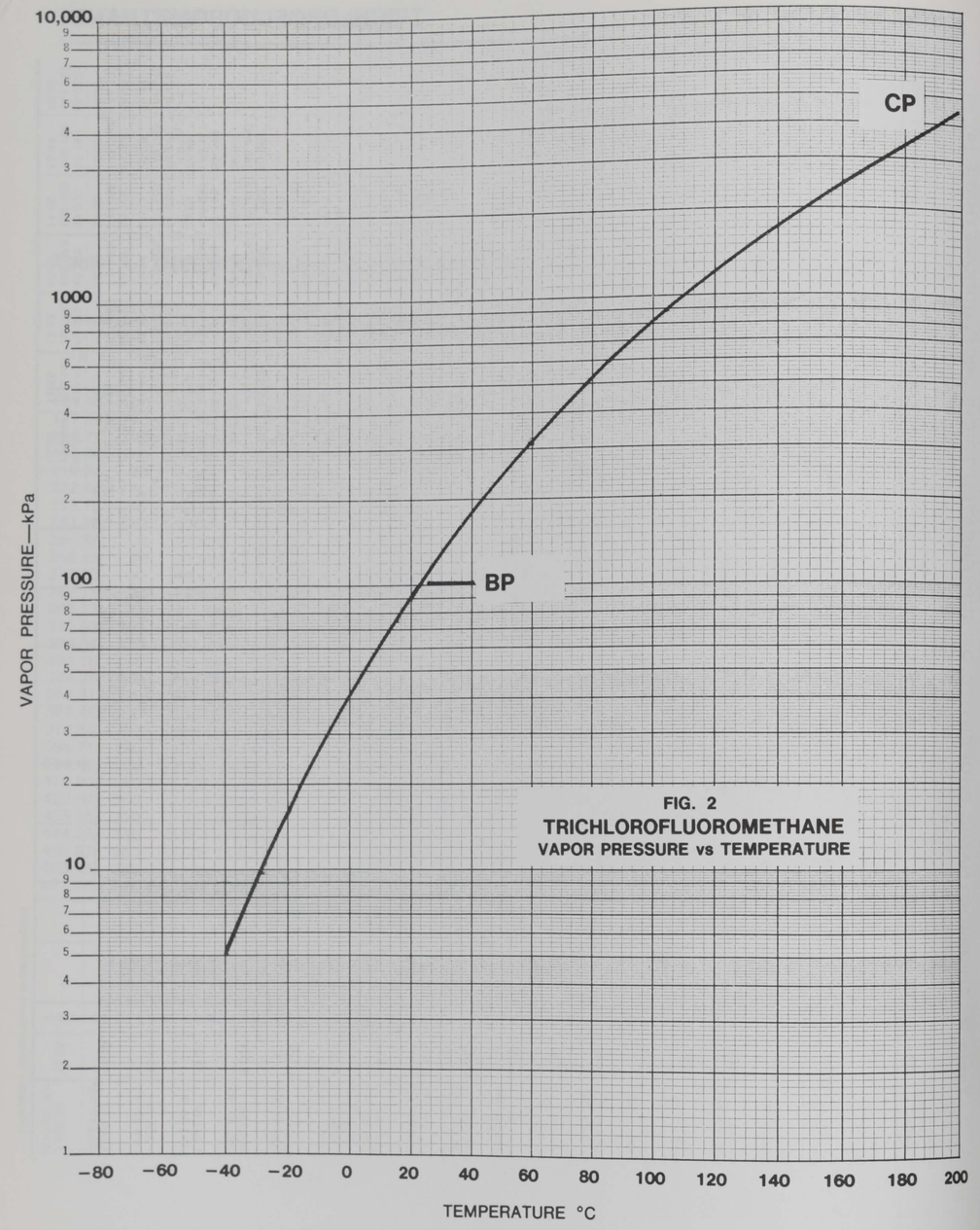


FIG. 2
TRICHLOROFLUOROMETHANE
VAPOR PRESSURE vs TEMPERATURE

1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE

(Synonym: Freon-113®)
(Formula: CCl_2FCClF_2)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	
One Mole of CCl_2FCClF_2	0.187 376 kg
Vapor Pressure @ 21.1 °C	0.187 376 kg
	37.9 kPa; 0.379 bar; 5.5 psia; 0.374 atm
Boiling Point @ 101.325 kPa	320.72 °K; 47.6 °C; 117.6 °F
Freezing Point	238.15 °K; −35.0 °C; −31.0 °F
Density, Saturated Vapor	7.38 kg/m³
Density, Liquid @ 25 °C	1.565 kg/l
Critical Temperature	487.25 °K; 214.1 °C; 417.4 °F
Critical Pressure	3 415 kPa; 34.15 bar; 495.3 psia; 33.7 atm
Critical Volume	1.734 dm³/kg
Critical Density	0.576 kg/dm³
Critical Compressibility Factor	0.274
Molar Specific Heat, Gas @ 101.325 kPa @ 60 °C	
@ Constant Pressure	126.221 J/(mol·°K)
@ Constant Volume	116.871 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 60 °C, Cp/Cv	1.080
Molar Specific Heat, Liquid @ 25 °C	170.887 J/(mol·°K)
Viscosity, Vapor @ 48.9 °C	0.010 8 mPa·s; 0.010 8 cP
Viscosity, Liquid @ Saturation Pressure @ 48.9 °C	0.497 mPa·s; 0.497 cP
Thermal Conductivity, Gas @ 50.7 kPa @ 25 °C	0.077 8 W/(m·°K); 18.6 × 10^{-6} cal·cm/(s·cm²·°C)
Thermal Conductivity, Liquid @ 25 °C	0.065 7 W/(m·°K); 157 × 10^{-6} cal·cm/(s·cm²·°C)
Surface Tension @ 25 °C	23 mN/m; 23 dyn/cm
Solubility In Water @ Saturation Pressure @ 25 °C	0.017% (by weight)
Refractive Index, Liquid, n_D @ 25 °C	1.354
Dielectric Constant, Liquid @ 25 °C	2.41

Description

At room temperature and atmospheric pressure, 1,1,2-Trichloro-1,2,2-trifluoroethane (denoted henceforth as TTE) is a water-white noncorrosive, nonflammable, volatile liquid. TTE has little odor in low concentrations; in high concentrations, its odor is ethereal and similar to carbon tetrachloride. TTE is shipped in drums and cans under its own vapor pressure of 37.9 kPa (5.5 psia) at 21.1 °C.

Specifications

TTE has a minimum purity of 99.0%.

Uses

TTE is used as a refrigerant, as a heat transfer medium, as a selective solvent for oils and gums, as an effective film processing solvent for both machine and hand use, and as an intermediate in the manufacture of chlorotrifluoroethylene.

Effects In Man and Toxicity (2)

Inhalation of high concentrations of gas can cause such symptoms as dizziness, disorientation, incoordination, narcosis, nausea, or vomiting. There appear to be no irreversible effects once the oxygen deficiency has been corrected.

TTE has relatively low toxicity. It is considerably less toxic than carbon tetrachloride. It is classified according to the rating system devised by Underwriters' Laboratories as much less toxic than Group 4 (which includes methyl chloride and ethyl bromide) and somewhat more toxic than group 5 (which includes carbon dioxide and butane). However, prolonged breathing of the vapor should be avoided, and TTE should be

used preferably in areas having adequate ventilation. Prolonged contact of TTE with the skin should be avoided, since it has a drying effect by dissolving the fats and oils from the skin. The 1979 American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a Threshold Limit Value of 1 000 ppm (7600 mg/m^3) for TTE.

First Aid Treatment (2)

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration and oxygen simultaneously. Treat symptomatically thereafter.

Precautions in Handling and Storage

Since TTE is a relatively nontoxic and nonflammable liquid of low vapor pressure, the usual precautions associated with the handling of compressed gases are not applicable. However, TTE should be handled in an adequately ventilated area. When the hands are to be exposed to liquid TTE for any extended period, it is desirable to wear rubber or neoprene gloves.

Leak Detection

A sensitive means of leak detection is afforded by the Matheson Gas Leak Detector, Models 8016 and 8017.

Materials of Construction

The commonly used metals, such as steel, cast iron, brass, copper, tin, lead, and aluminum, can be used satisfactorily with TTE under normal conditions of use. At high temperatures, however, some of the metals may act as catalysts for the decomposition of TTE. The tendency of metals to promote thermal decomposition of TTE is in the following general order: (least decomposition) inconel < 18-8 stainless steel < nickel < copper < 1340 steel < aluminum < bronze < brass < silver (most decomposition).

Magnesium alloys and aluminum containing more than 2% magnesium are not recommended for use in systems containing TTE where water may be present. Zinc is not recommended for use with TTE.

Plastics and polymers, in general, are little affected by TTE.

Synthetic rubber such as Neoprene-GN or Hycar-OR-15 is essentially unaffected, although there is a small amount of swelling of natural rubber.

Cylinder and Valve Description

TTE is supplied in DOT approved drums. Drums have a ¾ inch I.P.S. female outlet.

Recommended Controls

Because of the low pressure, it is recommended that the drum be used either with an ordinary globe or gate valve, or drum spigot valve.

Shipping Regulations

TTE is shipped as a nonflammable chemical and does not require any DOT shipping labels.

Commercial Preparation

Numerous fluorination procedures are described in the patent literature for the preparation of TTE, most of which concern catalytic fluorination of perhalo-olefins or alkanes with hydrogen fluoride. TTE has also been prepared by electrolysis of bromotrichloroethylene, lithium fluoride, and calcium fluoride in liquid hydrogen fluoride.

Chemical Properties

TTE is nonflammable and nonexplosive at ordinary temperatures. The apparent ignition temperature is 1 256 °F, but the combustion is very weak and the flame does not propagate through the vapor-air mixture. The rate of hydrolysis of TTE in pure water at 86 °F and 1 atm is 0.000 005 kg/l of water/year; its hydrolysis rate in water in the presence of steel at saturation pressure and 112 °F is 0.040 kg/l of water/year. With respect to thermal stability, a maximum temperature of 225 °F is recommended for continuous TTE exposure in the presence of oil, steel, and copper. The rate of decomposition of TTE at 400 °F in steel is 6% per year. In quartz, the temperature for the first trace of decomposition of TTE is at about 570 °F (at an exposure time of 30 seconds).

Thermodynamic and Detailed Physical Data

Infrared Spectrum

See Figure 1 for the infrared spectrum of gaseous TTE.

Vapor Pressure (3)

The vapor pressure of liquid TTE between 10.342 and 3 275.009 kPa is represented by the following equation:

$$\log_{10} p = 33.065\,5 - \frac{4\,330.98}{T} - 9.263\,5 \log_{10} T + 0.002\,053\,9T$$

in which p = psia and T = °R (= °F + 459.67).

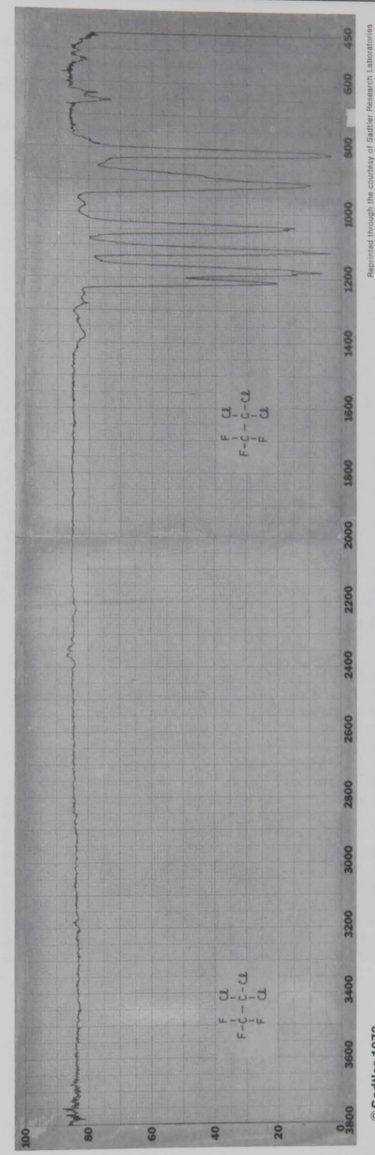
For specific vapor pressure data, see Table 1 and Figure 2.

Latent Heat of Vaporization, ΔHv @ 320.72 °K 27.494 kJ/mol; 35.07 kcal/kg

For additional ΔHv values, see Table 1.

Thermodynamic Data

Thermodynamic properties of the saturated liquid and vapor and of the superheated vapor are listed in Tables 1 and 2, respectively.



Reprinted through the courtesy of Sadtler Research Laboratories
© Sadtler 1972

Fig. 1. Infrared spectrum of gaseous TTE; 10-cm path length cell, with KBr optics; cell pressure (complete scan): 0.799 96 kPa (6 mmHg) (4).

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of 1,1,2-Trichloro-1,2,2-trifluoroethane, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, Lyndhurst, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 119–123, Matheson, Lyndhurst, New Jersey.

[3] A. F. Benning and R. C. McHarness, *Thermodynamic Properties of "Freon" 113, 1938*, Tech. Bull. T-113A, E. I. duPont de Nemours & Co., Inc., Wilmington, Delaware.

[4] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Table 1. THERMODYNAMIC PROPERTIES OF SATURATED TTE LIQUID AND VAPOR (3)

Temperature		Pressure		Entropy J/(mol·°K) (Base −40 °F)		Enthalpy kJ/mol (Base −40 °F)		Latent Heat of Vaporization kJ/mol	Specific Volume dm^3/kg		Density kg/dm^3	
°K	°F	kPa	atm	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
238.71	−30	2.059 4	0.020 3	3.685	136.256	0.858	32.513	31.655	0.591	5 135	1.692	0.000 20
244.26	−20	2.956 5	0.029 2	7.213	135.786	1.725	33.123	31.398	0.595	3 659	1.681	0.000 27
249.82	−10	4.168 6	0.041 1	10.741	135.472	2.596	33.742	31.146	0.599	2 652	1.669	0.000 38
255.37	0	5.775 7	0.057 0	14.268	135.237	3.476	34.360	30.884	0.603	1 955	1.658	0.000 51
260.93	10	7.874	0.078	17.640	135.080	4.355	34.983	30.628	0.607	1 464	1.647	0.000 68
266.48	20	10.577	0.104	21.011	135.002	5.240	35.606	30.366	0.611	1 112	1.637	0.000 90
272.04	30	14.003	0.138	24.303	135.002	6.132	36.237	30.105	0.616	855.9	1.623	0.001 17
277.59	40	18.306	0.181	27.596	135.080	7.038	36.869	29.831	0.621	666.7	1.610	0.001 50
283.15	50	23.628	0.233	30.810	135.237	7.944	37.505	29.561	0.626	526.0	1.597	0.001 90
288.71	60	30.158	0.298	34.025	135.472	8.863	38.141	29.278	0.631	419.1	1.585	0.002 39
294.26	70	38.080	0.376	37.239	135.707	9.791	38.781	28.990	0.636	337.4	1.572	0.002 96
299.82	80	47.588	0.470	40.375	136.099	10.727	39.421	28.694	0.641	274.2	1.560	0.003 65
305.37	90	58.916	0.581	43.511	136.491	11.673	40.061	28.388	0.646	224.7	1.548	0.004 45
310.93	100	72.257	0.713	46.568	136.883	12.626	40.702	28.076	0.652	185.8	1.534	0.005 38
316.48	110	87.977	0.868	49.704	137.354	13.598	41.346	27.748	0.657	154.6	1.522	0.006 47
322.04	120	106.179	1.048	52.762	137.824	14.582	41.991	27.409	0.664	129.7	1.506	0.007 71
327.59	130	127.208	1.255	55.819	138.373	15.571	42.636	27.065	0.670	109.5	1.493	0.009 13
333.15	140	151.202	1.492	58.799	139.000	16.572	43.276	26.704	0.676	93.08	1.479	0.010 74
338.71	150	178.781	1.764	61.856	139.549	17.587	43.912	26.325	0.683	79.47	1.464	0.012 58
344.26	160	209.876	2.071	64.835	140.176	18.615	44.552	25.937	0.690	68.30	1.449	0.014 64
349.82	170	244.971	2.418	67.814	140.803	19.652	45.183	25.531	0.697	58.94	1.435	0.016 97
355.37	180	284.202	2.805	70.794	141.430	20.701	45.815	25.114	0.704	51.15	1.420	0.019 55
360.93	190	328.190	3.239	73.694	142.136	21.764	46.442	24.678	0.712	44.54	1.404	0.022 45
366.48	200	376.867	3.719	76.673	142.763	22.844	47.069	24.225	0.720	38.96	1.389	0.025 67
372.04	210	430.922	4.253	79.574	143.469	23.938	47.692	23.754	0.728	34.19	1.374	0.029 25
377.59	220	490.010	4.836	82.475	144.174	25.039	48.311	23.272	0.736	30.13	1.359	0.033 19
394.26	250	701.886	6.927	88.041	144.409	27.383	49.600	22.217	0.762	21.16	1.312	0.047 26
422.04	300	1 210.72	11.95	101.682	147.467	33.023	52.331	19.308	0.824	11.86	1.214	0.084 32
449.82	350	1 953.28	19.28	115.794	149.348	39.251	54.356	15.105	0.918	6.55	1.089	0.152 7
455.37	360	2 136.00	21.08	118.460	149.427	40.497	54.609	14.112	0.949	5.81	1.054	0.172 1
460.93	370	2 330.43	23.00	122.615	150.132	42.030	54.722	12.692	0.974	5.06	1.027	0.197 6
466.48	380	2 537.96	25.05	124.575	148.408	43.406	54.522	11.116	1.018	4.31	0.982	0.232 0
472.04	390	2 758.59	27.23	127.554	147.388	44.822	54.195	9.373	1.068	3.68	0.936	0.271 7
477.59	400	2 994.39	29.55	130.062	145.429	46.072	53.407	7.335	1.136	3.06	0.880	0.326 8
483.15	410	3 244.67	32.02	132.336	141.665	47.187	51.682	4.495	1.242	2.43	0.805	0.411 5
487.26	417.4	3 439.79	33.95	133.198	133.198	47.688	47.688	0.000	1.735	1.735	0.576 4	0.576 4

Table 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED TTE VAPOR (3) H, ENTHALPY, kJ/mol; S, ENTROPY, J/(mol•°K); V, SPECIFIC VOLUME, dm^3/kg

Pressure kPa	Pressure atm		Temperature, °K 255.37	266.48	277.59	288.71	299.82	310.93	338.71	366.48	394.26	422.04	477.59	533.15
3.447 (246.71 K)*	0.034	H	34.365	35.623	36.904	38.206	39.526	40.867	44.308	47.875	51.577			
		S	139.470	144.331	149.035	153.660	158.129	162.519	173.103	183.216	192.938			
		V	3 282	3 425	3 568	3 713	3 857	4 000	4 357	4 715	5 072			
6.895 (258.48 K)*	0.068	H		35.619	36.895	38.197	39.517	40.858	44.304	47.871	51.569	55.384		
		S		138.608	143.312	147.859	152.328	156.796	167.380	177.493	187.215	196.544		
		V		1 709	1 781	1 852	1 924	1 996	2 176	2 355	2 535	2 713		
13.790 (271.71 K)*	0.136	H			36.882	38.180	39.500	40.841	44.291	47.858	51.555	55.380		
		S			137.432	142.057	146.526	150.995	161.579	171.692	181.413	190.743		
		V			887.1	923.3	959.5	995.7	1 086	1 176	1 265	1 355		
34.474 (291.87 K)*	0.340	H					39.452	40.798	44.243	47.823	51.521	55.345		
		S					138.843	143.233	153.817	164.009	173.730	183.138		
		V					380.6	395.1	431.5	468.0	504.5	540.3		
68.948 (309.59 K)*	0.680	H						40.715	44.169	47.749	51.455	55.288	63.324	
		S						137.275	147.937	158.129	167.850	177.258	195.133	
		V						195.0	213.5	232.0	250.3	268.6	305.1	
96.527 (319.21 K)*	0.953	H							44.108	47.697	51.403	55.245	63.289	
		S							145.037	155.228	165.028	174.436	192.311	
		V							151.1	164.5	177.8	191.0	217.3	
137.895 (330.15 K)*	1.361	H							44.012	47.614	51.325	55.170	63.228	
		S							141.901	152.092	161.892	171.300	189.253	
		V							104.4	114.1	123.4	132.8	151.5	
206.843 (343.76 K)*	2.041	H								47.461	51.190	55.049	63.132	
		S								148.486	158.286	167.772	185.725	
		V								74.54	81.09	87.52	100.1	
275.790 (354.21 K)*	2.722	H								47.309	51.050	54.931	63.032	
		S								145.821	155.699	165.185	183.216	
		V								54.88	59.91	64.80	74.54	
344.738 (362.87 K)*	3.402	H								47.156	50.915	54.809	62.928	71.534
		S								143.704	153.582	163.146	181.178	198.190
		V								43.07	47.21	51.23	59.18	66.92
413.685 (370.32 K)*	4.083	H									50.758	54.674	62.823	71.442
		S									151.857	161.422	179.532	196.622
		V									38.66	42.15	48.89	55.44
482.633 (376.93 K)*	4.763	H									50.610	54.548	62.718	71.355
		S									150.289	159.932	178.042	195.211
		V									32.57	35.64	41.55	47.26

* Saturation temperatures in parentheses.

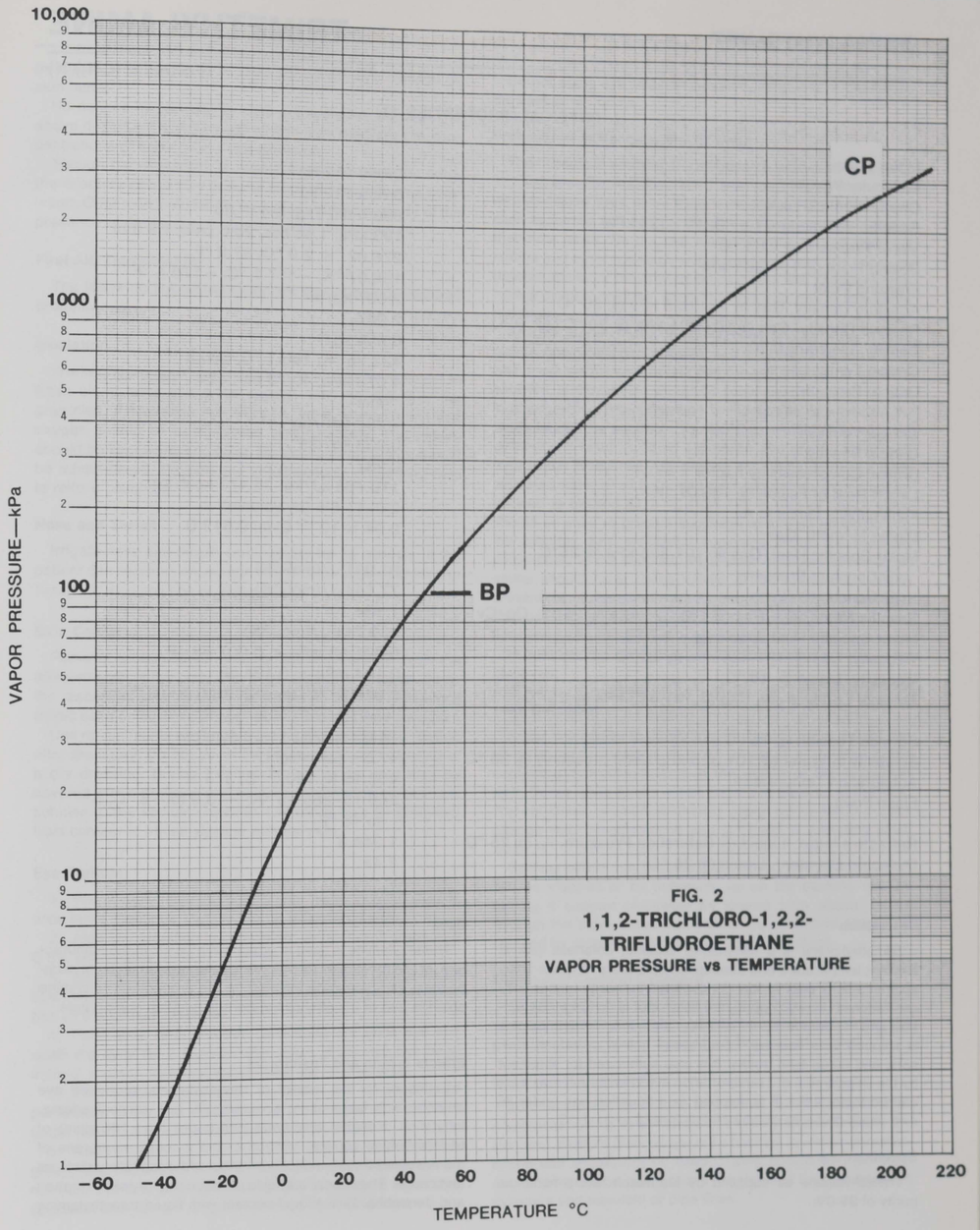


FIG. 2
1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE
VAPOR PRESSURE vs TEMPERATURE

TRIMETHYLAMINE

(Formula: $(CH_3)_3N$)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.059 112 kg
One Mole of $(CH_3)_3N$	0.059 112 kg
Specific Volume @ 21.1 °C, 101.325 kPa	399.5 dm^3/kg; 6.4 ft^3/lb
Vapor Pressure @ 21.1 °C	193 kPa; 1.93 bar; 28.0 psia; 1.9 atm
Boiling Point @ 101.325 kPa	276.02 °K; 2.9 °C; 37.2 °F
Freezing Point	156.07 °K; −117.1 °C; −178.4 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	2.607 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	2.087
Density, Liquid @ 0 °C	0.656 kg/l
Critical Temperature	433.25 °K; 160.1 °C; 320.2 °F
Critical Pressure	4 073 kPa; 40.73 bar; 590.7 psia; 40.2 atm
Critical Volume	4.297 dm^3/kg
Critical Density	0.233 kg/dm^3
Critical Compressibility Factor	0.287
Latent Heat of Fusion @ 156.07 °K	110.763 kJ/kg; 26.473 kcal/kg
Flammability Limits In Air	2.0–11.6% (by volume)
Dipole Moment, Gas	2.04×10^{-30} C·m; 0.612 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25°C	
@ Constant Pressure	91.931 J/(mol·°K)
@ Constant Volume	77.644 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.184
Molar Specific Heat, Liquid @ −2.7 °C	130.711 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.007 68 mPa·s; 0.007 68 cP
Viscosity, Liquid @ 15 °C	0.194 mPa·s; 0.194 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.015 06 W/(m·°K); 36.0×10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ 15 °C	14.53 mN/m; 14.53 dyn/cm
Solubility In Water @ 101.325 kPa (total pressure) @ 30 °C	47.5% (by weight)
Autoignition Temperature	463.15 K; 190.0 °C; 374 °F
Flash Point	260.15–265.15 °K; −13.0 to −8 °C; 8 to 18 °F
Refractive Index, Liquid @ Saturation Pressure, n_D @ 25 °C	1.344 3
Dielectric Constant, Liquid @ 25 °C	2.44

Description

Trimethylamine is a flammable, alkaline, colorless gas at ambient temperature and atmospheric pressure. It has a characteristic fishy odor in low concentrations, but in higher concentrations (100–500 ppm), the fishy odor is no longer detectable and the odor is more like that of ammonia. Trimethylamine is shipped as a liquefied compressed gas in cylinders, tank cars, and cargo tank trucks. It is also authorized for shipment by the Department of Transportation in ton multi-unit tank cars and portable tanks. It is shipped as a liquefied gas under its own vapor pressure of 92 kPa (13.3 psig) at 21.1 °C.

Specifications

Trimethylamine as supplied by Matheson has a minimum purity of 99.0%.

Uses

Trimethylamine is used in organic synthesis; in the manufacture of disinfectants; to prepare quaternary ammonium compounds; as a corrosion inhibitor; in the preparation of choline chloride and of trimethylamine-borane addition compounds.

Effects In Man and Toxicity (2)

Exposure to the vapors of trimethylamine produces eye irritation with lacrimation, conjunctivitis and corneal edema. Inhalation of higher concentrations (more than 100 ppm) of trimethylamine causes irritation of the mucous membrane of the nose and throat and lung irritation with respiratory distress and cough. The vapors may also produce primary skin irritation and dermatitis. Direct local contact with liquid trimethylamine produces severe and sometimes permanent eye damage or skin burns.

No definite human toxicity data are available, although the above described physiological effects from relatively low concentrations of vapor have been recorded.

Though trimethylamine is readily detectable in air by odor, the olfactory sense may become fatigued on continuous inhalation. Odor then is no longer a reliable warning property of the presence of dangerous concentrations of these vapors.

Matheson

First Aid Treatment (2)

The following suggested treatment should be administered promptly.

Inhalation

Workers overcome by trimethylamine should be removed to fresh air at once and given oxygen until the arrival of the physician. If breathing has stopped, artificial respiration and oxygen should be administered simultaneously. The patient should be kept warm and quiet. No alcoholic stimulants should be administered. Oxygen and antispasmodic drugs may help to relieve coughing.

Nose and Throat

Irrigate nose and mouth continuously for 15 minutes. If the patient can swallow, encourage him to drink large quantities of ½% citric acid solution or lemonade.

Skin Contact

Remove contaminated clothing and immediately flush the affected area of the body with large quantities of water. Since the reaction is alkaline, the skin should be washed with a mild acidic solution such as vinegar or 1–2% acetic acid solution.

Use no ointments on the skin during the first 24 hour period after the injury. Do not cover the injured area with clothing or a dry dressing. During the first 24 hours, the area may be covered with a dressing and kept moist with physiological salt solution (0.9% sodium chloride). Dermatitis may be produced from contact of trimethylamine with the skin.

Eye Contact

1. Immediately flush thoroughly with water, holding the lids wide open. Continue irrigation for at least 15 minutes.
2. After the irrigation is completed, instill 2 or 3 drops of a 0.5% pontocaine solution. This relieves the pain.
3. After the pain disappears (this may require a few minutes), flush the eyes with water or preferably physiological salt solution (0.9% sodium chloride).
4. Put 1 drop of fluorescein (eye-stain) into each eye and wash the eyes for 2 minutes with water. If the eye has been injured, a green stain will appear over the injured area.
5. If the eyeball stains green anywhere, put 1 more drop of pontocaine in the eye, wash the eye for 15 minutes (as shown under item 3) and restain with a drop of fluorescein.
6. Wash the eye for 2 minutes (item 3). If the eyeball stains green, take the patient to an eye specialist immediately, but do not stop the first aid treatment to take the patient to an eye specialist until items 1 through 6 have been completed.

Do not apply eye pads or pressure, as gluing of the lids to the eyeball will occur.

Precautions in Handling and Storage

The hazards in handling trimethylamine are due to its toxicity and extreme flammability. Store and use trimethylamine in a well-ventilated area away from heat and all ignition sources such as flames and sparks. Never use flames to detect trimethylamine leaks. Do not use trimethylamine around sparking motors and other non-explosion-proof equipment. Do not store reserve stocks of trimethylamine cylinders with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials.

Anyone working with trimethylamine should wear rubber gloves, chemical safety goggles, and a rubber or plastic apron. Gas masks approved by NIOSH for trimethylamine service, showers, and eyebaths should be conveniently located for use in emergencies.Trimethylamine cylinders should never be directly heated by steam or flames. Uncontrolled heating of a cylinder will result in liquid expansion and create dangerous hydrostatic pressures. Any heating should be done in a thermostated water or oil bath, and the temperature should not be allowed to exceed 51.7 °C (125 °F). A trap or check valve should be used to prevent suckback of foreign materials into the cylinder. Any accidental suckback should be reported immediately to the supplier. Manifolded cylinders of trimethylamine should have check valves at the cylinder outlets to prevent the exchange of material from one cylinder to another, thus causing a cylinder to become overfull. All equipment and lines used with trimethylamine should be grounded.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Never use flames to detect trimethylamine leaks. Leaks can be detected by passing an open bottle or a squeeze bottle containing hydrochloric acid in the vicinity of the suspected leak. Dense white fumes will be formed in the area of the leak. Wet ret litmus or phenolphthalein paper will undergo a color change with trimethylamine and is of aid in detecting small leaks.

Cylinder valves may develop leaks through the packing which can be stopped or by tightening up on the packing nut, by turning it counter clockwise as viewed from above. Leaks through the valve outlet that cannot be controlled should be stopped by plugging the outlet with ⅜″ pipe plugs.

Disposal of Leaking Cylinders

Should it ever become necessary to dispose of the contents of a leaking cylinder which cannot be stopped normally, the procedure described in Appendix II-B may be followed.

Materials of Construction

Iron, steel, stainless steel, and monel recommended for all equipment coming in contact with trimethylamine. Copper, tin, zinc and most of their alloys are attacked by moist trimethylamine and should not be used. Piping should be rigid steel except where short connections are required such as between cylinders and manifold or pipe lines.

For permanent installations, tongue and groove, flanged fittings with lead or asbestos composition gaskets are recommended. In order to reduce maintenance, all joints should be welded wherever possible.

Cylinder and Valve Description

Cylinder valves are made of forged steel and are of the packed type. The valve outlet designated as alternate standard for trimethylamine by the Compressed Gas Association (CGA) is connection No. 240. The thread specifications are ⅜"-18NGT-RH-INT accepting tapered threaded pipe. (See Figure 1 for the drawing and specifications on this valve outlet and its mating connection). Lecture bottles have a special 5/16"-32 threads per inch, female valve outlet.

Cylinders containing 15 lbs. or more of trimethylamine are equipped with goose neck dip-tubes. Withdrawal of vapor is accomplished by placing the cylinder in the normal vertical position. On occasion, a full cylinder standing in the sun will heat up and cause the liquid to expand and cover the end of the dip-tube. In this case, it is necessary to allow the cylinder to cool before the vapor can be withdrawn or the cylinder should be placed in a horizontal position with the valve outlet facing down.

To withdraw liquid the cylinder should be placed in a horizontal position with the valve outlet facing up.

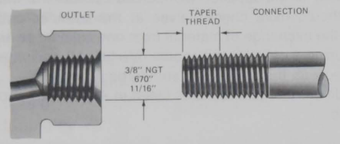


Fig. 1. CONNECTION 240 3/8"-NGT RH INT IPS accepting Tapered Threaded Pipe

Safety Devices

Since no safety devices are used in trimethylamine cylinders, extra precautions should be used to prevent cylinders from being exposed to heat, which could cause uncontrolled hydrostatic pressure build-up.

Recommended Controls

Automatic Pressure Regulators

Single stage regulator Model 13-240 is recommended for use with trimethylamine. The regulator has an anodized aluminum body with internal parts of type 316 stainless steel. The diaphragm is of FEP Teflon on Neoprene and the seat is Teflon. The regulator has a delivery pressure range of 28–240 kPa (4–35 psig).

Low pressure regulator Model 71-240 is available for sensitive and accurate low pressure control. The regulator has an oversized, pancake, aluminum body, type 303 stainless steel nozzle and needle valve outlet, a Teflon-faced Butyl rubber diaphragm, a Teflon seat, and a delivery pressure range of 3.4–34.5 kPa (0.5–5.0 psig).

Manual Controls

Matheson supplies a type 303 stainless steel needle valve, Model 61-240, for direct attachment to the cylinder valve outlet and suitable for manual flow control of the liquid or vapor phase. This valve may be equipped with a variety of outlets, such as a hose connection, ¼" tube fitting, or ¼" male or female pipe. A Model 32S or Model 59 stainless steel manual needle valve is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the intrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless or pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Trimethylamine is classified by the DOT as a flammable, compressed gas and is shipped with the required "Red Gas Label".

Commercial Preparations

Trimethylamine is produced by the interaction of methanol and ammonia over a catalyst at high temperature. Mono-, di-, and trimethylamines are all produced by this process. Yields are regulated by the conditions employed.

Chemical Properties

Trimethylamine gives an alkaline reaction in aqueous solution and forms salts with acids. When heated with alkyl or aralkyl halides, it forms quaternary ammonium salts. Trimethylamine does not react with acetic anhydride, acetyl chloride, or benzenesulfonyl chloride (as differentiated from primary and secondary amines).

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

A C_{3v} equilibrium molecular symmetry has been established for trimethylamine, with the following structural parameters:

Matheson

bond distances: C—N 1.451 Å (1.451×10^{-10} m); C—H_s 1.109 Å (1.109×10^{-10} m); C—H_a 1.088 Å (1.088×10^{-10} m); bond angles: N—C—H_s 111.7°; H_a—C—H_s 108.1°; C—N—C 110.9°; N—C—H_a 110.1°; H_a—C—H_a 108.6° (see Figure 2 for notation of H_a and H_s).

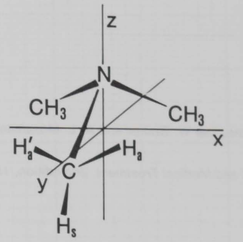


Fig. 2. Equilibrium conformation of the methyl groups in trimethylamine. H_a and H'_a specify the two equivalent out-of-plane hydrogen positions on the same methyl group (3).

Infrared Spectrum

See Figure 3 for the infrared spectrum of gaseous trimethylamine.

Vapor Pressure (4)

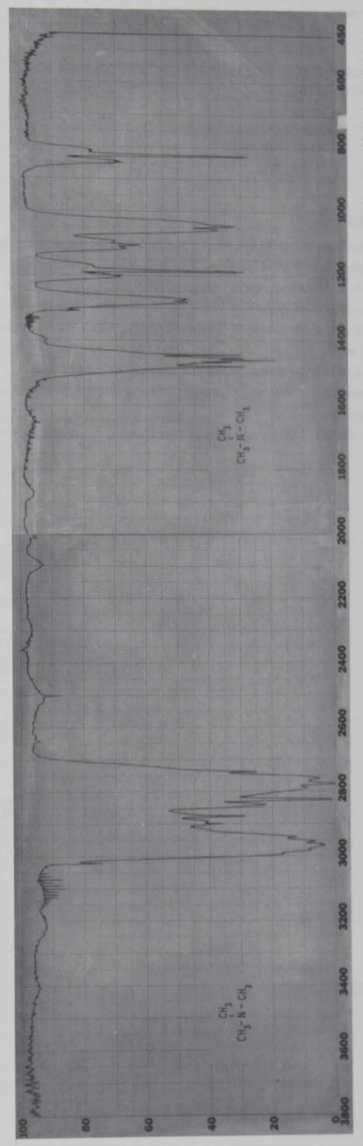
The vapor pressure of liquid trimethylamine in the range of 192.825–276.594 °K (−80.325 °C to 3.444 °C) is shown below.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
192.825	0.805	8.05	6.04
199.059	1.367	13.7	10.25
210.801	3.354	33.5	25.16
221.202	6.777	67.8	50.83
226.298	9.305	93.1	69.79
231.366	12.548	125.5	94.12
237.523	17.684	176.8	132.64
244.633	25.624	256.2	192.20
250.073	33.494	334.9	251.23
257.166	46.505	465.1	348.82
264.155	63.039	630.4	472.83
270.027	80.208	802.1	601.61
273.920	93.495	935.0	701.27
276.068	101.526	1 015	761.51
276.594	103.611	1 036	777.15

For vapor pressure data, see Figure 4.

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/mol
250.00	24.376
276.02	22.951
318.15	20.610



©Sadtler 1972

Reprinted through the courtesy of Sadtler Research Laboratories

Fig. 3. Infrared spectrum of gaseous trimethylamine; 10-cm path length cell, with KBr optics; cell pressure (complete scan): 2.000 kPa (15 mmHg) (7).

Matheson

TRIMETHYLAMINE

Thermodynamic Properties of Trimethylamine As Ideal Gas @ 25 °C			
Heat Capacity, C_p° (5)	91.755 J/(mol·°K)	Enthalpy Difference, $H_{298}^\circ - H_{273}^\circ$(5)	2.224 kJ/mol
Heat Capacity, S°(5)	91.755 J/(mol·°K)	Enthalpy of Formation, ΔH_f°(6)	−24.31 kJ/mol
		Gibbs Energy of Formation, ΔG_f°(6)	98.95 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of trimethylamine, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 51–55, Matheson, Lyndhurst, New Jersey.

[3] J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.* 51, 1580–1583 (1969).

[4] J. G. Aston, *et al.*, *J. Amer. Chem. Soc.* 66, 1171 (1944).

[5] K. A. Kobe and R. H. Harrison, *Petroleum Refiner* 33, 161 (1954).

[6] D. D. Wagman, *et al.*, *Selected Values of Chemical Thermodynamic Properties, 1968*, p. 167, NBS Tech. Note 270-3, U. S. Government Printing Office, Washington, D. C.

[7] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

Matheson

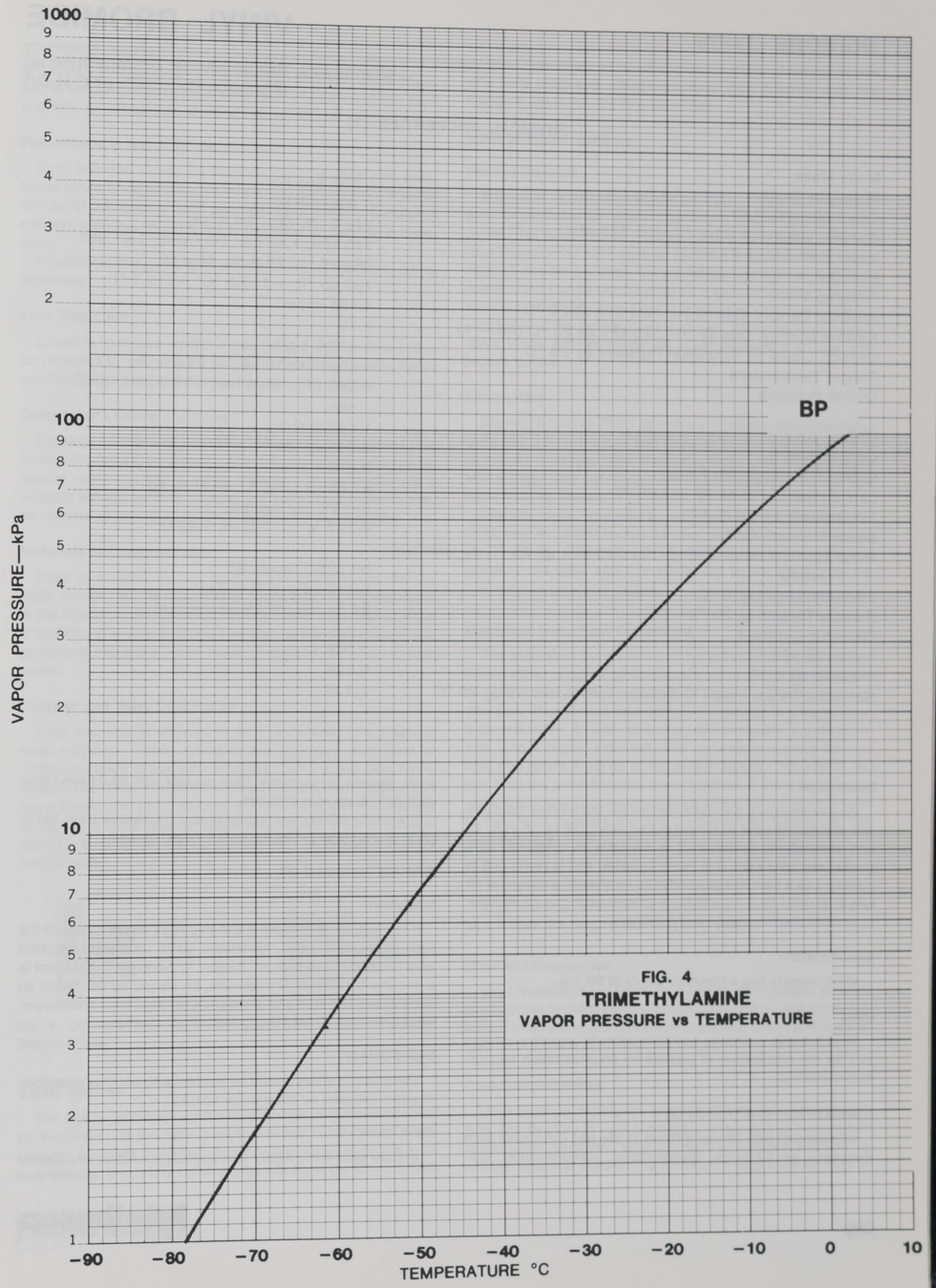


FIG. 4
TRIMETHYLAMINE
VAPOR PRESSURE vs TEMPERATURE

VINYL BROMIDE

(Synonyms: Bromoethene; Bromoethylene)
(Formula: CH_2:CHBr or C_2H_3Br)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.106 955 kg
One Mole of C_2H_3Br	0.106 955 kg
Specific Volume @ 21.1 °C, 101.325 kPa	218.5 dm^3/kg; 3.5 ft^3/lb
Vapor Pressure @ 21.1 °C	143 kPa; 1.43 bar; 20.7 psia; 1.41 atm
Boiling Point @ 101.325 kPa	288.95 °K; 15.8 °C; 60.4 °F
Freezing Point	133.65 °K; −139.5 °C; −219.1 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	4.485 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	3.79
Density, Liquid @ Saturation Pressure @ 25 °C	1.473 8 kg/l
Critical Temperature	463.51 °K; 190.4 °C; 374.6 °F
Critical Pressure	6 860 kPa; 68.6 bar; 994.9 psia; 67.7 atm
Critical Volume	1.445 dm^3/kg
Critical Density	0.692 kg/dm^3
Critical Compressibility Factor	0.275
Latent Heat of Fusion @ 133.65 °K	47.865 kJ/kg; 11.44 kcal/kg
Flammability Limits In Air	9–14% (by volume)
Dipole Moment, Gas	4.737×10^{-30} C·m; 1.42 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	55.535 J/(mol·°K)
Viscosity, Liquid @ 0 °C	0.419 mPa·s; 0.419 cP
Surface Tension @ 20 °C	22.54 mN/m; 22.54 dyn/cm
Dielectric Constant	
Gas @ 100 °C	1.008 1
Liquid @ 5 °C	5.628
Refractive Index, Liquid @ Saturation Pressure, n_D @ 25 °C	1.435

Description

Vinyl bromide is a colorless, flammable, moderately toxic gas with a pleasant odor at temperatures over 289.15 °K (16 °C) and atmospheric pressure. It is available in cylinders, tank trucks, and tank cars. It is easily liquefied and is reshipped in cylinders as a liquefied gas under its own vapor pressure of 41 kPa (6 psig) at 21.1 °C with 0.1% phenol added as an inhibitor to prevent polymerization in the cylinder.

Specifications

Vinyl bromide has a minimum purity of 99.5%.

Uses

Vinyl bromide is used as an intermediate in organic synthesis and for the preparation of plastics by polymerization and copolymerization.

Effects In Man and Toxicity (2)

Inhalation of high concentrations of this gas can cause such symptoms as dizziness, disorientation, incoordination, narcosis, nausea, or vomiting. Skin contact with liquid vinyl bromide can cause skin irritation.

The 1979 ACGIH has established a Threshold Limit Value (TLV) of 250 ppm (1100 mg/m^3) for vinyl bromide.

First Aid Treatment (2)

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration and oxygen simultaneously. Treat symptomatically thereafter.

Skin Contact

The affected areas should be washed with copious quantities of water followed by soap water solution.

Eye Contact

Irrigate eyes immediately with copious quantities of water for at least 15 minutes holding the eyelids apart during the irrigation to insure contact of the water with all tissues of the eyes and lids. An eye specialist should be called promptly.

Matheson

Precautions in Handling and Storage

Vinyl bromide should be handled in a well-ventilated area, preferably a hood with forced ventilation. Do not store reserve stocks of cylinders of vinyl bromide with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks in lines and equipment containing vinyl bromide may be detected by painting the suspected points with soap water solution; leaks will be indicated by bubble formation.

Disposal of Leaking Cylinders

Leaking cylinders of vinyl bromide should be removed to a hood with forced ventilation. After attaching the appropriate needle valve and check valve, introduce the contents into a suitable solvent such as toluene or xylene. Vinyl bromide may be recovered from the resulting solution by fractionation.

Materials of Construction

Steel is satisfactory for handling vinyl bromide in the dry state. Copper and its alloy should not be used as it might result in the formation of explosive acetylides from trace impurities of acetylene. Wet vinyl bromide may also be handled in steel, but prolonged exposure under these conditions will result in corrosion.

Cylinder and Valve Description

Vinyl bromide is shipped in DOT approved, low pressure steel cylinders. These cylinders are equipped with steel or cadmium-plated brass valves having Compressed Gas Association (CGA) valve outlet connection No. 290. The valve outlet has a thread size of 0.745 inch, with left-hand external threads accepting a bullet-shaped nipple (see Figure 1 for an illustration). Lecture bottles have a special $\frac{5}{16}$"-32 threads per inch, female outlet.

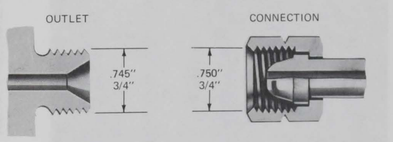


Fig. 1. CONNECTION 290 .745"-14 LH EXT. accepting a Bullet Shaped Nipple

Safety Devices

The most commonly used safety device, and the one used by Matheson, is the spring-loaded safety relief valve. If the cylinder pressure becomes dangerously high, usually due to overheating, the safety relief device will open (at about 2 590 kPa (375 psig) and release gaseous vinyl bromide until the pressure again returns to a safe level.

Recommended Controls

Manual Controls

Matheson needle valve Model 61-290, of type 303 stainless steel is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets (¼" tube fitting or ¼" NPT male or female pipe or a hose connection). It should be used only where manual flow control is needed and should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. Stainless steel needle valve Model 32S or Model 59 is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electric mass flowmeters, such as Matheson Series No. 8116 and No. 8160 should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Vinyl bromide, inhibited, is shipped as nonflammable chemical. It does not require DOT shipping labels.

Chemical Preparation

Vinyl bromide is prepared by addition of hydrogen bromide to acetylene in the presence of catalysts and by dehydrobromination of ethylene dibromide with alcoholic potassium hydroxide.

Chemical Properties

Vinyl bromide undergoes polymerization and copolymerization. The Br atom in vinyl bromide is unreactive in nucleophilic substitution reactions. Vinyl bromide undergoes addition reactions similar to olefins. The inhibitor in vinyl bromide may be

Matheson

removed by scrubbing with dilute caustic solution or by fractional distillation.

Magnesium reacts with a saturated solution of vinyl bromide in tetrahydrofuran at 40–50 °C to form the Grignard reagent vinylmagnesium bromide. Vinyl bromide may be converted to vinyllithium by reaction with phenyllithium. Reaction of vinyl bromide and arsenic in the presence of copper and zinc as catalysts yields a mixture of products including $CH_2 = CHAsBR_2$, $(CH_2 = CH)_2AsBr$, and $AsBr_3$. Aromatic Grignard reagents react with vinyl bromide in the presence of cobaltous chloride or chromous chloride to give fair yields of normal condensation products, e.g., $CH_2 = CHBr + C_6H_5MgBr \rightarrow CH_2 = CHC_6H_5 + MgBr_2$.

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

The planar vinyl bromide molecule has the following structural parameters; bond distances: C═C 1.34 Å (1.34×10^{-10} m); C—Br 1.86 Å (1.86×10^{-10} m); C—H 1.08 Å (1.08×10^{-10} m); bond angles: C—C—Br 120°; C—C—H 120°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous vinyl bromide.

Vapor Pressure (4)

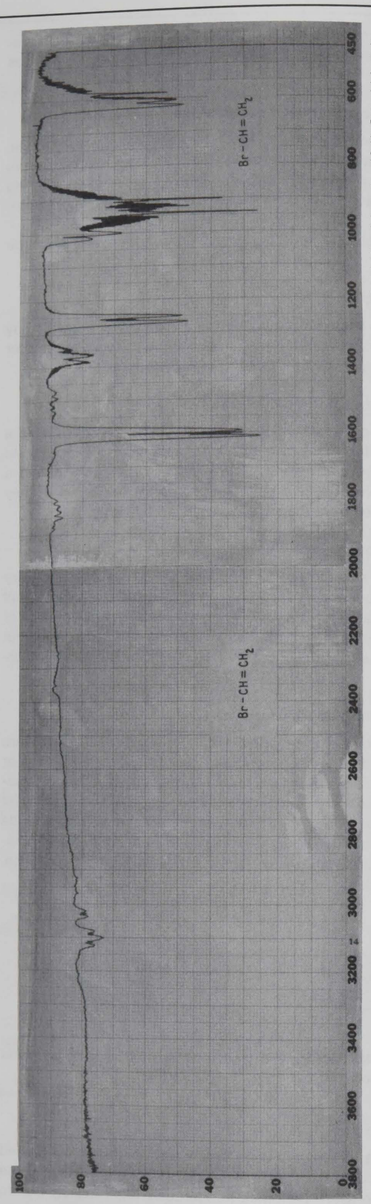
The vapor pressure of liquid vinyl bromide from 183.15 °K to 310.15 °K is shown below.

	Vapor Pressure		
Temperature, °K	kPa	mbar	mmHg
183.15	0.213	2.13	1.6
193.15	0.453	4.53	3.4
203.15	1.013	10.1	7.6
213.15	2.133	21.3	16.0
223.15	4.000	40.0	30.0
233.15	7.466	74.7	56.0
243.15	13.066	130.7	98.0
253.15	23.331	233.3	175
263.15	37.997	380.0	285
273.15	57.328	573.3	430
283.15	87.993	880.0	660
293.15	133.322	1 333	1 000
303.15	213.315	2 133	1 600
310.15	266.644	2 666	2 000

See Figure 3 for vapor pressure curve.

Latent Heat of Vaporization, ΔHv (4)

Temperature, °K	ΔHv, kJ/mol
273.15	25.209
283.15	24.644
288.95	24.267



Reprinted through the courtesy of Sadtler Research Laboratories
©Sadtler 1972

Fig. 2. Infrared spectrum of gaseous vinyl bromide; 10-cm path length cell, with KBr optics; cell pressure (complete scan): 2.666 kPa (20 mmHg) (5).

Thermodynamic Properties of Vinyl Bromide As Ideal Gas @ 25 °C (4)			
Heat Capacity, C_p°	55.522 J/(mol·°K)	Free Energy Function, $(F_{298}^\circ - H_{298}^\circ)/298$	−275.433 J/(mol·°K)
Entropy, S°	275.433 J/(mol·°K)	Enthalpy of Formation, ΔH_f°	78.366 kJ/mol
		Free Energy of Formation, ΔF_f°	80.676 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of vinyl bromide, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, 1977, pp. 119–123, Matheson, Lyndhurst, New Jersey.

[3] R. E. Richards, *J. Chem. Soc. 1948*, 1931–1933.

[4] *Vinyl Bromide*, Tech. Bull. 125-669-66. 1966. The Dow Chemical Co., Midland, Michigan.

[5] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

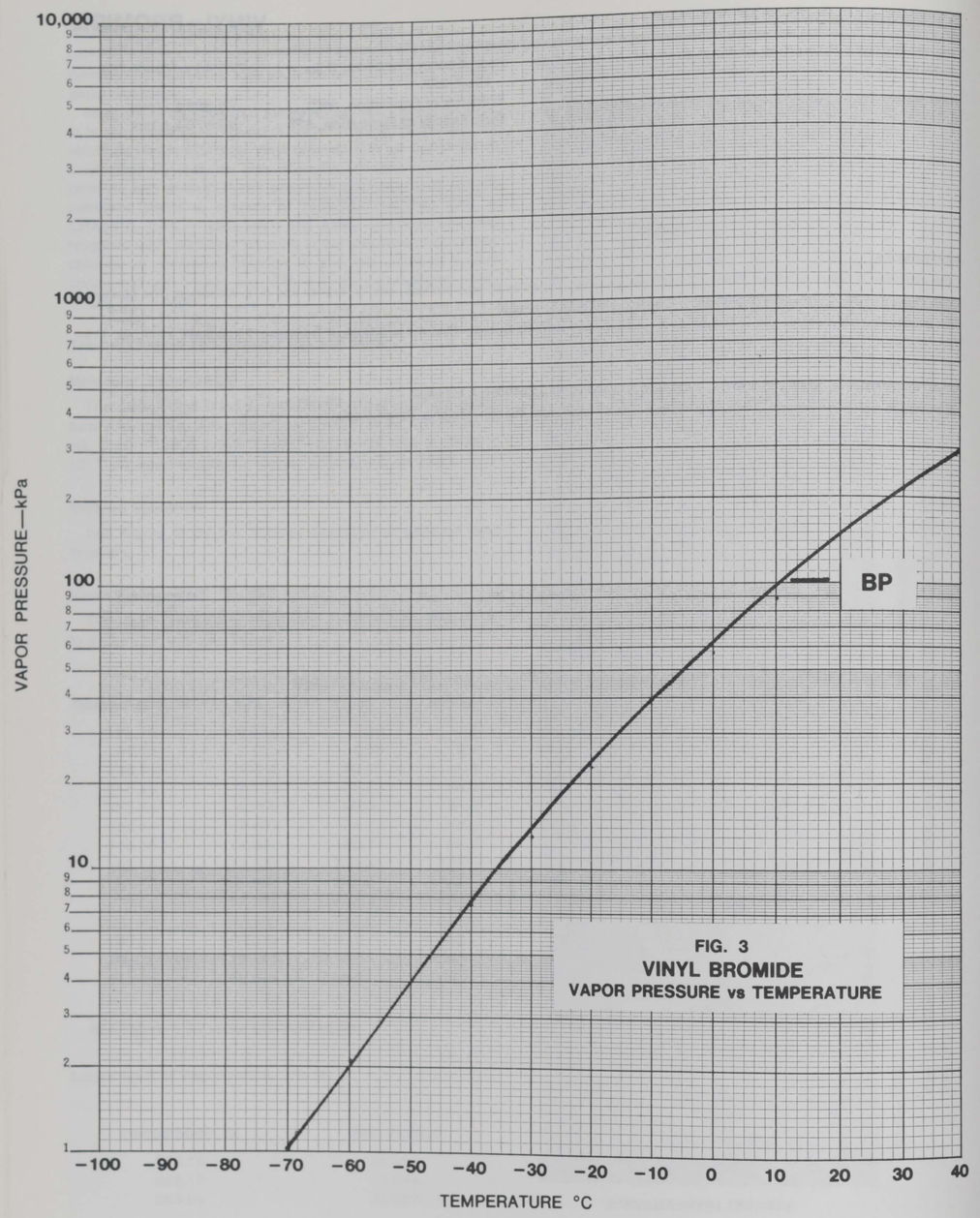


FIG. 3
VINYL BROMIDE
VAPOR PRESSURE vs TEMPERATURE

Matheson

VINYL CHLORIDE

(Synonyms: Chloroethene; Chloroethylene)
(Formula: CH_2:CHCl or C_2H_3Cl)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.062 499 kg
One Mole of C_2H_3Cl	0.062 499 kg
Specific Volume @ 21.1 °C, 101.325 kPa	387.0 dm^3/kg; 6.2 ft^3/lb
Vapor Pressure @ 21.1 °C	336 kPa; 3.36 bar; 48.7 psia; 3.31 atm
Boiling Point @ 101.325 kPa	259.35 °K; −13.8 °C; 7.2 °F
Freezing Point	119.45 °K; −153.7 °C; −244.7 °F
Absolute Density, Gas @ 101.325 kPa @ 25 °C	2.620 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	2.21
Density, Liquid @ −20 °C	0.972 kg/l
Critical Temperature	424.61 °K; 151.5 °C; 304.6 °F
Critical Pressure	5 755 kPa; 57.55 bar; 834.7 psia; 56.8 atm
Critical Volume	2.71 dm^3/kg
Critical Density	0.369 kg/dm^3
Critical Compressibility Factor	0.276
Latent Heat of Fusion @ 119.45 °K	75.90 kJ/kg; 18.14 kcal/kg
Flammability Limits In Air	4–22% (by volume)
Dipole Moment, Gas	4.837×10^{-30} C·m; 1.45 D
Molar Specific Heat, Gas @ 101.325 kPa @ 25 °C @ Constant Pressure	53.607 J/(mol·°K)
Molar Specific Heat, Liquid @ 0 °C	78.449 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 20 °C	0.010 72 mPa·s; 0.010 72 cP
Viscosity, Liquid @ −20 °C	0.280 mPa·s; 0.280 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.007 95 W/(m·°K) 19.0×10^{-6} cal/cm/(s·cm^2·°C)
Surface Tension @ −20 °C	23.1 mN/m; 23.1 dyn/cm
Solubility In Water @ 101.325 kPa (total pressure) @ 25 °C	1.07 cm^3/1.0 ml water
Refractive Index, Liquid @ Saturation Pressure, n_D @ 25 °C	1.366
Dielectric Constant, Liquid @ 27.2 °C	6.26
Autoignition Temperature	745.15 °K; 472.0 °C; 882.0 °F
Flash Point	195.15 °K; −78.0 °C; −108.4 °F

Description

Vinyl chloride is a colorless, highly flammable gas having a pleasant, sweet odor in high concentrations. Vinyl chloride is toxic and carcinogenic; at this writing a TLV standard of 5 ppm has been established. It is shipped in cylinders, single-unit tank cars, and ton multiunit tank cars, and in tank trucks and ton multiunit tanks on trucks. It is readily liquefied and is reshipped in steel cylinders as a liquefied compressed gas under its own vapor pressure 234 kPa (34 psig) at 21.1 °C. It is shipped with an inhibitor (phenol) to prevent polymerization in the cylinder.

Specifications

Vinyl chloride typically has a minimum purity of 99.9 mole% (liquid phase).

Uses

Vinyl chloride is used as an intermediate in organic synthesis and for the production of plastics by polymerization and co-polymerization.

Effects In Man and Toxicity (2)

The 1979 ACGIH has established a Threshold Limit Value (TLV) of 5 ppm (10 mg/m^3) for vinyl chloride.

It has been reported that concentrations of above 1 000 ppm slowly produce mild disturbances such as drowsiness, blurred vision, staggering gait, and tingling and numbness in the feet and hands.

The carcinogenicity of vinyl chloride has been established after notification that several workers who handled and used

Matheson

vinyl chloride developed a rare form of liver cancer. Exposure of rats to vinyl chloride by inhalation at and below 500 ppm induced tumors, including angiosarcomas of the liver. Another series of experiments on the effect of exposure of rats, mice and hamsters to vinyl chloride at concentrations of 10 000; 6 000; 2 500; 500; 250; and 50 ppm have been carried out for varying periods of time. The experimental results so far reported are that tumors have been observed in groups of animals exposed to vinyl chloride at concentrations as low as 250 ppm.

Liquid vinyl chloride on skin contact may cause severe irritation and burns.

First Aid Treatment

Summon a physician at once for anyone who has been exposed to high concentrations of vinyl chloride vapor or its liquid state.

Inhalation

The victim, especially if he complains of dizziness, should be removed to an uncontaminated, well-ventilated room. Oxygen should be administered, by trained personnel only. The patient should be kept quiet and comfortably warm but not hot and a physician summoned.

Skin Contact

Remove contaminated clothes and shoes and wash the affected areas with copious quantities of water followed by soap water solution.

Eye Contact

Irrigate the eyes immediately with copious quantities of water for at least 15 minutes, holding the eyelids apart during the irrigation to insure contact of the water with all tissues of the eyes and lids. An eye specialist should be called promptly.

Precautions in Handling and Storage

An effective educational and training program should be instituted to inform the workers of the hazards involved in handling and using vinyl chloride, and the first aid measures to be followed in the event of an emergency. Vinyl chloride should be used in a well-ventilated area, preferably a hood with forced ventilation. All lines and equipment to contain vinyl chloride should be grounded. Personnel handling vinyl chloride should wear safety shoes, chemical safety gogles and/or a full face shield, and rubber gloves. For respiratory protection, self-contained breathing equipment, air-line gas masks and U.S. Bureau of Mines approved cannister type gas masks should be available in emergencies. Instant-acting safety showers and eye fountains should be conveniently located near the site of the operation. Store and use cylinders of vinyl chloride in well-ventilated area away from heat and all sources of ignition such as flames and sparks. Do not use vinyl chloride around sparking motors or other non-explosion proof equipment. Do not store reserve stocks of cylinders of vinyl chloride with cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks of vinyl chloride in lines and equipment may be detected by applying soap water solution to the suspected sites; leaks will be indicated by bubble formation.

Analytical Detection

Matheson has available a Toxic Gas Detector, Model 8014K, for detection of 0.25–10 ppm vinyl chloride in the atmosphere (Model 8014-132SC detector tube). A 100-cm^3 sample of the atmosphere is drawn into the detector tube which contains a chemical reagent that absorbs and reacts with vinyl chloride. A color stain is produced which varies in length with the concentration. The length of the stain is read directly off the detector tube scale.

Disposal of Leaking Cylinders

Leaking cylinders of vinyl chloride that cannot be corrected normally may be handled in the following manner. Put on an appropriate gas mask or self-contained breathing equipment and place the cylinder in a hood with forced ventilation. Attach an appropriate regulator and check valve to the cylinder valve outlet. Introduce the vinyl chloride at a moderate rate into an adequate amount of a suitable solvent such as carbon tetrachloride, chloroform, 1,2-dichloroethane, or chlorobenzene. The resulting solution can be fractionated for recovery of vinyl chloride.

Materials of Construction

Steel is a completely satisfactory material for handling vinyl chloride. Copper and its alloys should not be used as it might result in the formation of explosive acetylides from trace impurities of acetylene. Fittings and connections for 1.5 inch and larger pipe should be flanged or butt welded. Fittings and connections for 1 inch and smaller pipe may be threaded and the appropriate joint compound used. Garlock No. 7021, 1/16 inch thick asbestos gaskets, or equivalent are satisfactory for flanged connections. Teflon, lead, and carbon are also suitable.

Cylinder and Valve Description

Vinyl chloride is shipped in DOT approved, low pressure steel cylinders. Cylinders of vinyl chloride are equipped with steel or cadmium-plated brass valves having Compressed Gas Association (CGA) valve outlet connection No. 290. The valve outlet has a thread size of 0.745 inch, with left-hand external threads accepting a bullet-shaped nipple (see Figure 1 for an illustration of the valve outlet and its mating connection). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet.

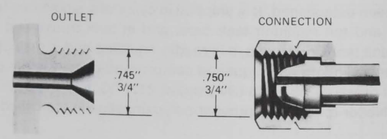


Fig. 1. CONNECTION 290 .745"-14 LH EXT. accepting a Bullet Shaped Nipple

Safety Devices

The most commonly used device, and the one used by Matheson, is the spring-loaded safety relief valve. If the cylinder pressure becomes dangerously high usually due to overheating, the safety relief device will open (at about 2 590 kPa (375 psig)) and release gaseous vinyl chloride until the pressure again returns to a safe level.

Recommended Controls

Automatic Pressure Regulators

Matheson regulator Model 13-290 is recommended for use with vinyl chloride. This single stage regulator has an anodized aluminum body, type 316 stainless steel internal parts, a diaphragm of FEP Teflon on Neoprene and a Teflon seat. It has a delivery pressure range of 28–240 kPa (4–35 psig).

Low pressure regulator Model 71-290 is available for sensitive and accurate low pressure control. The regulator has an oversized, pancake, aluminum body, type 303 stainless steel internal parts, a Teflon-faced Butyl rubber diaphragm, a Teflon seat, and a delivery pressure of 3.4–34.5 kPa (0.5–5.0 psig).

Manual Controls

Matheson needle valve Model 61-290, of type 303 stainless steel, is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets, such as a connection hose, 1/4" inch tube fitting, or 1/4 inch NPT male or female connection. It should be used only where manual flow control is needed and should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. Stainless steel needle valve Model 32S or Model 59 is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150mm tubes and floats or Matheson Series 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series No. 8116 and No. 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes, and flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Vinyl chloride, inhibited, is classified by the DOT as a flammable compressed gas and is shipped with the "Red Gas Label".

Commercial Preparation

Vinyl chloride is made by the catalyzed addition of HCl to acetylene, by thermal decomposition of ethylene chloride, or by heating the latter with alcoholic caustic alkali.

Chemical Properties

Vinyl chloride is readily polymerized to polyvinyl chloride by a variety of methods. It also may be copolymerized with other unsaturated compounds. The Cl atom in vinyl chloride is unreactive in nucleophilic substitution reactions. Vinyl chloride undergoes addition reactions similar to the olefins. The inhibitor in cylinder vinyl chloride may be removed by scrubbing with dilute caustic solution, or by fractional distillation.

Thermodynamic and Detailed Physical Data

Molecular Structure

The planar vinyl chloride molecule has the following structural parameters: bond distances: C=C 1.355 Å (1.355 × 10^{-10} m); C-Cl 1.728 Å (1.728 × 10^{-10} m); C-H 1.078 Å (1.078 × 10^{-10} m); bond angles: C-C-Cl 121.1°; C-C-H 126°.

The lack of reactivity of the chlorine atom in vinyl chloride, CH_2=CHCl, is attributed to resonance involving the polarized structure $\overset{-}{CH_2}\text{-}CH{=}\overset{+}{Cl}$. The resonance effect is such that the chlorine atom is bound to the carbon atom by a linkage which has double bond character and the chlorine atom therefore is less labile than in the normal C-Cl bond. Vinyl chloride has a dipole moment of 1.45 D.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous vinyl chloride.

Vapor Pressure (5)

The vapor pressure of liquid vinyl chloride up to 101.325 kPa (1 atm) is shown below.

Temperature, °K	Vapor Pressure		
	kPa	mbar	mmHg
167.55	0.133	1.33	1
182.35	0.667	6.67	5
189.45	1.333	13.3	10
197.45	2.666	26.7	20
206.35	5.333	53.3	40
212.05	7.999	80.0	60
219.95	13.332	133	100
231.85	26.664	267	200
245.15	53.329	533	400
259.35	101.325	1 013.25	760

The vapor pressure above 101.325 kPa (1 atm) is tabulated below (6).

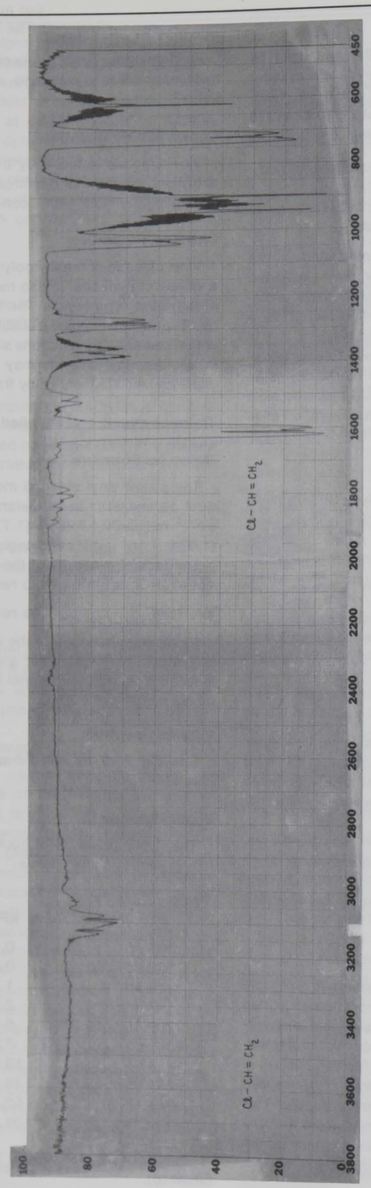


Fig. 2. Infrared spectrum of gaseous vinyl chloride; 10-cm path length cell, with KBr optics; cell pressure (complete scan) 5.333 kPa (40 mmHg) (8).

Matheson

Temperature, °K	Vapor Pressure kPa	bar	atm
283.15	254.326	2.54	2.51
293.15	343.492	3.43	3.39
303.15	466.095	4.66	4.60
313.15	583.632	5.84	5.76
323.15	733.593	7.34	7.24
333.15	924.084	9.24	9.12
343.15	1 137.880	11.38	11.23

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/kg
213.15	388.8
233.15	376.2
259.35	357.29

Thermodynamic Data

Compressibility data for vinyl chloride are shown in Table 1.

Thermodynamic Properties of Vinyl Chloride As Ideal Gas @ 25 °C (7)

Heat Capacity, C_p°	53.723 J/(mol·°K)
Entropy, S°	263.885 J/(mol·°K)
Free Energy Function, $(G_{298}^\circ - E_0^\circ)/298$	−224.221 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	11.820 kJ/mol
Enthalpy of Formation, ΔH_f°	35.564 kJ/mol
Free Energy of Formation, ΔG_f°	51.882 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of vinyl chloride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book*, *1975*, Matheson, East Rutherford, New Jersey.

[2] *The Toxic Substances List*, H. E. Christiansen, T. T. Luginbyhl, and B. S. Carroll, *1974*, pp. LXXIX–LXXXI, Federal Register, Volume 39, No. 67, National Institute for Occupational Safety and Health, Rockville, Maryland.

[3] *Federal Register*, Volume 39, No. 194, Oct. 4, 1974, National Institute for Occupational Safety and Health, Rockville, Maryland.

[4] R. C. Ivey and M. I. Davis, *J. Chem. Phys.* 57, 1909–1911, (1972).

[5] *Chemical Engineers' Handbook*, 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p. 3–61, McGraw-Hill Book Co., Inc., New York, New York.

[6] J. T. Rozlooskaya and M. I. Temkin, *J. Appl. Chem.* (U.S.S.R.) 19, 32 (1946).

[7] D. D. Wagman, *et al.*, *Selected Values of Chemical Thermodynamic Properties*, *1968*, p. 143, Natl. Bur. Stand. Tech. Note-270-3, U. S. Government Printing Office, Washington, D. C.

[8] *The Sadtler Standard Spectra*, *1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

[9] W. Hayduk and H. Laudie, *J. Chem. Eng. Data* 19, 253–257, (1974).

Matheson

Table 1. COMPRESSIBILITY FACTORS Z, FOR GASEOUS VINYL CHLORIDE (9)

Temperature, 273.15 °K Pressure			Temperature, 323.15 °K Pressure		
kPa	atm	Z	kPa	atm	Z
52.689	0.52	0.988	101.325	1.00	0.985
101.325	1.00	0.974	190.491	1.88	0.969
119.564	1.18	0.969	330.320	3.26	0.948
142.868	1.41	0.956	419.486	4.14	0.932
167.186	1.65	0.933	574.513	5.67	0.900
173.266	1.71	0.905	731.566	7.22	0.850
			807.560	7.97	0.700
Temperature, 298.15 °K Pressure			**Temperature, 348.15 °K Pressure**		
kPa	atm	Z	kPa	atm	Z
101.325	1.00	0.981	101.325	1.00	0.988
144.895	1.43	0.975	228.994	2.26	0.972
169.213	1.67	0.969	345.518	3.41	0.954
230.008	2.27	0.961	447.856	4.42	0.939
298.909	2.95	0.945	615.043	6.07	0.911
345.518	3.41	0.916	812.626	8.02	0.869
369.836	3.65	0.888	1 033.515	10.20	0.808
395.168	3.90	0.846			

VINYL FLUORIDE

(Synonyms: Fluoroethene; Fluoroethylene)
(Formula: CH_2:CHF or C_2H_3F)

PHYSICAL PROPERTIES (1)

Molar Mass	
Molecular Weight	0.046 044 kg
One Mole of C_2H_3F	0.046 044 kg
Specific Volume @ 21.1 °C, 101.325 kPa	524.4 dm^3/kg; 8.4 ft^3/lb
Vapor Pressure @ 21.1 °C	2 549 kPa; 25.49 bar; 369.7 psia; 25.16 atm
Boiling Point @ 101.325 kPa	200.95 °K; −72.2 °C; −98.0 °F
Melting Point	112.65 °K; −160.5 °C; −256.9 °F
Absolute Density, Gas @ 101.325 kPa @ 20 °C	1.924 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 20 °C (Air = 1)	1.60
Density, Liquid @ −80 °C	0.879 kg/l
Critical Temperature	327.85 °K; 54.7 °C; 130.5 °F
Critical Pressure	5 239 kPa; 52.39 bar; 759.9 psia; 51.7 atm
Critical Volume	3.127 dm^3/kg
Critical Density	0.320 kg/dm^3
Critical Compressibility Factor	0.277
Flammability Limits In Air	2.6–21.7% (by volume)
Dipole Moment, Gas	4.77×10^{-30} C.m; 1.43 D
Molar Specific Heat, Liquid @ −80 °C	51.24 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 25 °C	0.010 8 mPa·s; 0.010 8 cP
Viscosity, Liquid @ −80 °C	0.184 mPa·s; 0.184 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 25 °C	0.011 17 W/(m·°K) 26.7 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ −80 °C	0.106 7 W/(m·°K) 255 × 10^{-6} cal·cm/(s·cm^2·°C)
Surface Tension @ −80 °C	20.6 mN/m; 20.6 dyn/cm
Autoignition Temperature	733 °K; 460 °C; 860 °F
Refractive Index, Liquid @ Saturation Pressure, n_D @ 25 °C	1.34

Description

Vinyl fluoride is a colorless, flammable, nontoxic gas with a faint ethereal odor at ambient temperature and atmospheric pressure. It is available in cylinders, tank trucks, and tank cars. It is reshipped in cylinders as a liquefied compressed gas under its own vapor pressure of 2 448 kPa (355 psig) at 21.1 °C. Vinyl fluoride is inhibited with 0.2% Terpene B, a complex mixture of terpenes. Inhibited vinyl fluoride has excellent stability.

Specifications

Vinyl fluoride has a typical minimum purity of 99.9%. It contains less than 10 ppm acetylene and less than 10 ppm oxygen. Vinyl fluoride is inhibited with 0.2% Terpene B, a complex mixture of terpenes.

Uses

Vinyl fluoride is of interest as a chemical intermediate. It can be polymerized to form a homopolymer, and it can also be copolymerized with other monomers.

Effects in Man and Toxicity (2)

Inhalation of high concentrations of this gas can cause such symptoms as dizziness, disorientation, incoordination, narcosis, nausea, or vomiting. There appear to be no irreversible effects once the oxygen deficiency has been corrected.

Skin contact with liquid vinyl fluoride can cause irritation or frostbite.

Vinyl fluoride is relatively nontoxic. According to the rating system devised by the Underwriters' Laboratories, Chicago, Illinois, vinyl fluoride falls into Groups 5A or 6 in this system. Group 5A includes those gases or vapors which are much less toxic than those in Group 4 but much more toxic than those in Group 6. Group 4 includes those gases or vapors which in concentrations of about 2–2.5% for durations of exposure of about 2 hours are lethal and produce serious injury. Group 6 contains those gases or vapors which in concentrations up to at least 20% by volume in air for durations of exposure for about 2 hours do not appear to produce injury. The relatively nontoxic carbon dioxide is classified as a Group 5A gas by Underwriters' Laboratories.

First Aid Treatment (2)

Inhalation

If the subject is conscious and becomes aware of any of the symptoms cited above, he should go to an uncontaminated area and inhale fresh air or oxygen. In the event the subject is overcome by a massive exposure, he should be carried to an uncontaminated area and given artificial respiration and oxygen simultaneously. Treat symptomatically thereafter.

Skin Contact

In case of skin contact with liquid vinyl fluoride, frostbite may develop. If frostbite occurs, cover the frostbitten part with a warm hand or woolen material. If the fingers or hand are frostbitten, have the victim hold his hand in his armpit, next to his body. Then place the frostbitten part in warm water, about 42 °C (108 °F). If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Let the circulation re-establish itself naturally. Encourage the victim to exercise the affected part while it is being warmed.

Precautions in Handling and Storage

Vinyl fluoride is hazardous because of its extreme flammability. All lines and equipment to contain vinyl fluoride should be grounded. Store and use vinyl fluoride in well-ventilated areas away from heat and all sources of ignition such as flames and sparks. Do not use flames to detect leaks, use soap water solution. Do not use vinyl fluoride around sparking motors or other non-explosion-proof equipment. Do not store reserve stocks of cylinders containing oxygen, chlorine, or other highly oxidizing or flammable materials.

In addition, the general rules listed in Appendix I should be observed.

Leak Detection

Leaks of vinyl fluoride in lines and equipment may be detected by applying soap water solution to the suspected points. Leaks will be evident by bubble formation.

Disposal of Leaking Cylinders

For disposal procedure see Appendix II-A.

Alternatively, the contents of a leaking cylinder could be disposed of by introducing the gas at a moderate rate into an adequate amount of a solution of bromine in carbon tetrachloride (conversion to 1,2-dibromo-1-fluoroethane), after first attaching an appropriate regulator and check valve to the cylinder valve outlet.

Materials of Construction

Steel is completely satisfactory for handling vinyl fluoride. Copper should not be used because of possible formation of explosive acetylides from trace impurities of acetylene. Systems should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

Vinyl fluoride is shipped in DOT approved steel cylinders. Cylinders of vinyl fluoride are equipped with brass valves having Compressed Gas Association (CGA) valve outlet connection Model 320. The valve outlet has a thread size of 0.825 inch, with right-hand external threads with a flat seat and using a washer as a seal (see Figure 1 for details and dimensions). Lecture bottles have a special 5/16 inch-32 threads per inch, female outlet.

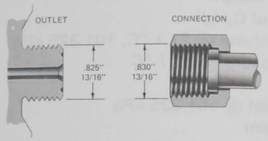


Fig. 1. CONNECTION 320 .825"-14 RH EXT. used with Flat Seat and Washer

Safety Devices

Cylinders of vinyl fluoride have frangible discs as safety devices. They should, therefore, be stored away from sources of heat to prevent the development of pressure capable of rupturing the disc.

Recommended Controls

Automatic Pressure Regulators

Matheson automatic regulator Model 12-320, constructed of an aluminum body, Teflon seat, type 316 stainless steel internal parts, and FEP Teflon coated Neoprene diaphragm, is recommended for use with vinyl fluoride. This single stage regulator has a delivery pressure range of 28–550 kPa (4–80 psig). It is provided with a delivery pressure gauge only, since the cylinder pressure will remain constant as long as liquid remains in the cylinder.

Matheson regulator Model 71-320 is available for low pressure delivery (delivery pressure range 3.4–34.5 kPa (0.5–5.0 psig)). This regulator is constructed of an aluminum body and a Teflon-faced Butyl rubber diaphragm.

Manual Controls

Matheson needle valve Model 61-320 of type 303 stainless steel is available for direct attachment to the cylinder valve outlet. This valve may be equipped with a variety of outlets such as a hose connection, ¼" tube fitting, or ¼" NPT male or female connection. It should be used only where manual flow control is needed and should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed. Stainless steel needle valve Model 32S or Model 59 is recommended for use with lecture bottles.

Flowmeters

Matheson Series 7600 laboratory stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series Model 8116 and Model 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure change. Flow rates may be recorded from the instrument's electrical output.

Matheson

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Vinyl fluoride, inhibited, is classified by the DOT as a flammable compressed gas and is shipped with the required "Red Gas Label".

Commercial Preparations

Vinyl fluoride is produced from acetylene and hydrogen fluoride in the presence of mercury catalysts. Another method is the addition of hydrogen fluoride to acetylene to form 1,1-difluoroethane, followed by pyrolysis of the latter.

Chemical Properties

Vinyl fluoride undergoes typical olefinic reactions. It can be polymerized to form a homopolymer and it can be copolymerized with other monomers. The Terpene B inhibitor must be removed before using vinyl fluoride for polymerization. This is best done by passing the vinyl fluoride vapor from a cylinder through silica gel.

Thermodynamic and Detailed Physical Data

Molecular Structure (3)

Vinyl fluoride is a planar molecule, with a C═C bond distance of 1.313 Å (1.313×10^{-10} m) and H-C-F bond angle of 114°.

Infrared Spectrum

See Figure 2 for the infrared spectrum of gaseous vinyl fluoride.

Vapor Pressure (4)

The vapor pressure of liquid vinyl fluoride up to its boiling point is shown below.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
123.85	0.133	1.33	1
135.15	0.667	6.67	5
140.95	1.333	13.3	10
147.75	2.666	26.7	20
155.15	5.333	53.3	40
160.15	7.999	80.0	60

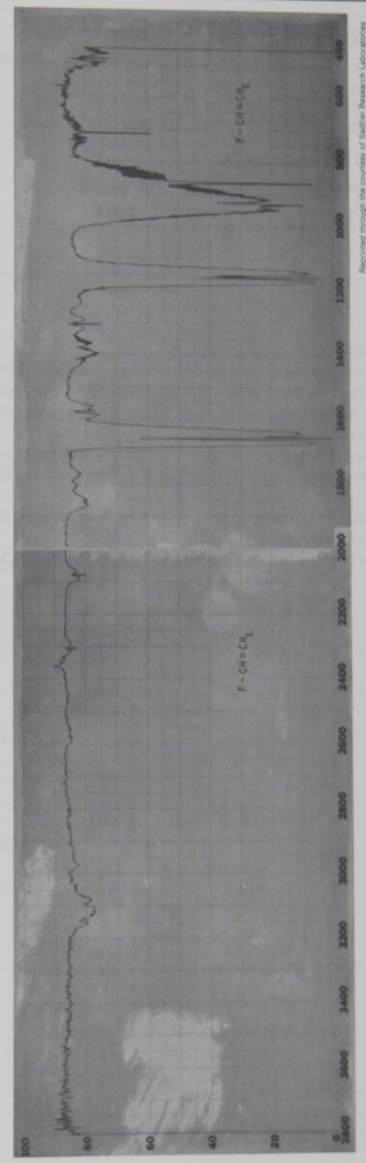


Fig. 2. Infrared spectrum of gaseous vinyl fluoride, 10-cm path length cell, with °KBr optics; cell pressure (complete scan): 4,000 kPa (30 mmHg) (6).

VINYL FLUORIDE

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
166.95	13.332	133	100
177.75	26.664	267	200
189.15	53.329	533	400
200.95	101.325	1 013.25	760

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/mol
173.15	17.916

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/mol
193.15	16.992
200.95	16.606

Thermodynamic Properties of Vinyl Fluoride As Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	50.459 J/(mol·°K)
Entropy, S°	252.63 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	11.347 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of vinyl fluoride, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 119–123, Matheson, Lyndhurst, New Jersey.

[3] M. Avram and G. D. Mateescu, *Infrared Spectroscopy, 1972*, pp. 168–176, John Wiley & Sons, Inc., New York, New York.

[4] **Chemical Engineers' Handbook,** 5th edition, R. H. Perry and C. H. Chilton, editors, *1973*, p. 3–61, McGraw-Hill Book Co., Inc., New York, New York.

[5] D. D. Wagman, *et al, Selected Values of Chemical Thermodynamic Properties, 1968*, Natl. Bur. Stand. Tech. Note 270-3, U. S. Government Printing Office, Washington, D. C.

[6] *The Sadtler Standard Spectra, 1972*, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

XENON

(Formula: Xe)

PHYSICAL PROPERTIES (1)

Atomic Mass	
Atomic Weight	0.131 30 kg
One Mole of Xe	0.131 30 kg
Specific Volume @ 21.1 °C, 101.325 kPa	180.0 dm^3/kg; 2.9 ft/lb
Boiling Point @ 101.325 kPa	165.014 °K; −108.1 °C; −162.6 °F
Triple Point	
Temperature	161.25 °K; −111.9 °C; −169.4 °F
Pressure	82 kPa; 0.82 bar; 0.81 atm
Absolute Density, Gas @ 101.325 kPa @ 25 °C	5.391 kg/m^3
Relative Density, Gas @ 101.325 kPa @ 25 °C (Air = 1)	4.553
Density, Liquid @ Saturation Pressure @ 161.4 °K	3.084 kg/l
Critical Temperature	289.74 °K; 16.6 °C; 61.9 °F
Critical Pressure	5 838 kPa; 58.38 bar; 846.7 psia; 57.62 atm
Critical Volume	0.904 8 dm^3/kg
Critical Density	1.105 2 kg/dm^3
Critical Compressibility Factor	0.288
Latent Heat of Fusion @ 161.25 °K	17.48 kJ/kg; 548.5 cal/mol
Dipole Moment, Gas	0 C·m
Molar Specific heat, Gas @ 101.325 kPa @ 25 °C	
@ Constant pressure	21.012 J/(mol·°K)
@ Constant Volume	12.658 J/(mol·°K)
Specific Heat Ratio, Gas @ 101.325 kPa @ 25 °C, Cp/Cv	1.66
Molar Specific Heat, Liquid @ 163–166 °K	44.56 J/(mol·°K)
Viscosity, Gas @ 101.325 kPa @ 300 °K	0.023 24 mPa·s; 0.023 24 cP
Viscosity, Saturated Liquid @ 289.74 °K	0.528 mPa·s; 0.528 cP
Thermal Conductivity, Gas @ 101.325 kPa @ 20	0.005 61 W/(m·°K) 13.4 × 10^{-6} cal·cm/(s·cm^2·°C)
Thermal Conductivity, Liquid @ 165.014 °K	0.073 22 W/(m·°K) 175 × 10^{-6} cal·cm/(s·cm^2·°C)
Solubility In Water @ Xenon partial pressure of 101.325 kPa @ 15.1 °C	0.123 6 cm^3 Xe/1 ml water
Dielectric Constant, Gas @ 25 °C and 101.325 kPa	1.001 238
Refractive Index, Gas @ 101.325 kPa, n_D @ 25 °C	1.000 642
First Ionization Potential	1 943.2 × 10^{-21} J; 12.129 eV
Velocity of Sound In Gaseous Xenon @ 0 °C and 101.325 kPa	168 m/s

Description

Xenon is a member of Group VIIIA elements, which have been called noble gases, inert gases, and aerogens. Xenon is a colorless, odorless, and tasteless monatomic gas. It exists in very minute traces in the atmosphere (8.6 × 10^{-2} ppm by volume). Xenon is commonly available in small cylinders at pressures up to 5 520 kPa (800 psig). It is also available in 1 l quantities in glass flasks.

Specifications

Matheson supplies two grades of xenon.

1. Research Purity Grade

This grade has a typical minimum purity of 99.995 mol %.

2. C.P. Grade

This grade has a minimum purity of 99.9 mol %.

Uses

Xenon is used to a limited extent in the lighting and electronic industry. Xenon is used as a light source for specialized applications. An important application of xenon is as a fill for thyratron and half-wave rectifier tubes.

Effects in Man (2)

The coordinating capacity of the nervous system is impaired by even slight degrees of oxygen deficiency; the subject can not think clearly or control his limbs accurately. The development of symptoms depends on the degree and duration of the oxygen deficiency and also on the rapidity with which the deficiency is developed. In sudden and acute asphyxia, unconsciousness is immediate. When the asphyxia develops slowly enough the following symptoms appear: increased volume of breathing, accelerated pulse rate, muscular incoordination, faulty judgment, emotional instability, fatigue, fainting, nausea, vomiting, bewilderment, respiration in gasps.

No Threshold Limit Value (TLV) has been recommended for xenon, which is proposed to be a simple asphyxiant.

First Aid Treatment (2)

If the subject is conscious and becomes aware of symptoms of asphyxia, he should go to an uncontaminated area and inhale fresh air or oxygen.

An unconscious subject must be carried to an uncontaminated area and given artificial respiration with simultaneous administration of oxygen as promptly as possible.

Few, even those who have been severely asphyxiated and who have not died during the asphyxiation, fail to make complete recoveries after receiving oxygen inhalation. Treat symptomatically thereafter.

Precautions in Handling and Storage

The general rules listed in Appendix I should be observed.

Materials of Construction

Since xenon is inert no special materials of construction are required. However, any piping or vessels containing xenon should be adequately designed to withstand the pressures to be encountered.

Cylinder and Valve Description

Xenon is packaged in DOT approved, steel cylinders. The cylinder valve outlet designated as standard by the Compressed Gas Association (CGA) is Model 580. This valve has a thread size of 0.965 inch, with right-hand internal threads accepting a bullet-shaped nipple (see Figure 1 for an illustration).

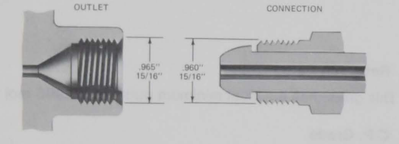


Fig. 1. CONNECTION 580 .965"-14 RH INT. accepting a Bullet Shaped Nipple

Recommended Controls

Automatic Pressure Regulators

Single stage metal diaphragm regulators Model 19-580 and Model 3500-580 are recommended with both grades of xenon.

The Model 19-580 regulator is recommended for applications requiring low diffusion and leakage rates. The regulator has a brass body, German silver diaphragm, nylon seat, aluminum and nylon gaskets, and a diaphragm packless outlet valve with ¼" inch Gyrolok tube fitting. It has a delivery pressure range of 28–345 kPa (4–50 psig).

The Model 3500-580 regulator is especially designed for high purity systems requiring all stainless steel construction. All metal parts in the gas stream are of type 316 stainless steel. The diaphragm is stainless steel, the seat is Tefzel, the gaskets are Teflon, and the regulator has a diaphragm packless outlet valve with ¼ inch Gyrolok tube fitting. It has a delivery pressure range of 28–520 kPa (4–75 psig).

Both regulators can be supplied with a helium leak rate certification, the maximum acceptable leak rate being 2×10^{-9} cm^3 and 2×10^{-10} cm^3 for the Model 19-580 and Model 3500-580, respectively.

Two stage regulators Model 3104-580 and Model 3800-580 are also available for use with both grades of xenon.

The Model 3104-580 regulator has a brass body, type 302 stainless steel diaphragm, Tefzel seat, Teflon and nylon gaskets, and a diaphragm packless outlet valve with ¼ inch Gyrolok tube fitting. It has a delivery pressure range of 28–690 kPa (4–100 psig). The regulator can be optionally supplied with a helium leak rate certification, the maximum acceptable leak rate being 2×10^{-9} cm^3.

The Model 3800-580 regulator has a type 316 stainless steel body, type 316 stainless steel diaphragm, Tefzel seat, Kel-F and Teflon gaskets, and a diaphragm packless outlet valve with ¼ inch Gyrolok tube fitting. It has a delivery pressure range of 28–620 kPa (4–90 psig). It can be optionally supplied with a helium leak rate certification, the maximum acceptable leak rate being 2×10^{-9} cm^3.

Manual Controls

Diaphragm packless control valve Model 4351-580 is available for direct attachment to the cylinders. The valve is constructed of chrome plated brass and has a ¼ inch Gyrolok outlet connection.

This valve should be used only where flow control is constantly supervised and should not be used as a pressure control since it will not prevent pressure from building up if a system becomes clogged or if the system itself is closed.

Flowmeters

Matheson Series 7600 laboratory brass or stainless steel flowmeter units with 150 mm tubes and floats or Matheson Series 7200 laboratory brass or stainless steel flowmeter units with 65 mm tubes with a single float are recommended for use where definite flow rates must be known.

Electronic mass flowmeters, such as Matheson Series Model 8116 and Model 8160, should be used where accurate readings are required. Calibration is unaffected by temperature and pressure changes. Flow rates may be recorded from the instrument's electrical output.

Electronic Mass Flow Controllers

The Matheson Series 8240 of type 316 stainless steel and Series 8260 of type 316 stainless steel or monel are designed to control the flow of gas regardless of pressure and temperature changes. These mass flow controllers consist of a transducer, a control valve, a blind controller/power supply, a potentiometer, and a digital indicator. The transducer senses the gas flow and sends a signal to the power supply. This signal and one from the potentiometer are compared. If there is an imbalance, the power supply generates a signal for the control valve to reduce or increase the flow to correct the imbalance. The accuracy is ± 1.2%.

Shipping Regulations

Xenon is classified by the DOT as a nonflammable compressed gas and is shipped with the required "Green Label".

Commercial Preparation

Xenon is available only from the atmosphere and is obtained by the liquefaction and fractionation of large quantities of air.

Chemical Properties

While xenon is practically inert chemically, several xenon fluorides, XeF_2, XeF_4, and XeF_6 have been isolated by reaction of xenon and fluorine. A number of xenon-oxygen compounds have been prepared from the fluorides.

Thermodynamic and Detailed Physical Data

Atomic Structure

The xenon atom has a valence shell of eight electrons which is a closed octet. The closed shell is extremely stable and results in xenon being relatively inert chemically, although a difluoride, tetrafluoride, and hexafluoride as well as an oxytetrafluoride have been prepared. Xenon has an atomic radius of 2.2 Å (2.2×10^{-10} m).

Vapor Pressure

The vapor pressure of liquid xenon in the range 158.07–177.83 °K is represented by the following Antoine vapor pressure equation (3):

$$\log_{10} p = A - \frac{B}{C + t} \quad \text{or} \quad t = \frac{B}{A - \log_{10} p} - C$$

in which p = mmHg and t = °C, and the constants A, B, and C have the values of 6.642 89, 566.282, and 258.660, respectively.

Some calculated vapor pressures are shown below.

Temperature, °K	Vapor Pressure kPa	mbar	mmHg
158.07	66.661	667	500
161.015	79.993	800	600
163.598	93.326	933	700
165.014	101.325	1 013.25	760
165.910	106.658	1 067	800
168.010	119.990	1 200	900
169.939	133.322	1 333	1 000
173.392	159.987	1 600	1 200
177.83	199.984	2 000	1 500

Vapor pressure values between 180 and 290 °K are listed below (4).

Temperature, °K	Vapor Pressure kPa	bar	atm
180	217.849	2.18	2.15
200	506.625	5.1	5.0
220	1 013.250	10.1	10.0
240	1 874.512	18.7	18.5
260	3 090.412	30.9	30.5
280	4 762.275	47.6	47
290	5 876.850	58.8	58

Latent Heat of Vaporization, ΔHv

Temperature, °K	ΔHv, kJ/kg
165.014	96.1
161.25	97.1

Thermodynamic Data

Thermodynamic properties of real gas xenon and compressibility data are shown in Tables 1 and 2, respectively.

Thermodynamic Properties of Xenon As Ideal Gas @ 25 °C (5)

Heat Capacity, C_p°	20.786 J/(mol·°K)
Entropy, S°	169.579 J/(mol·°K)
Free Energy Function, $(F_{298}^\circ - H_0^\circ)/298$	−148.793 J/(mol·°K)
Enthalpy Difference, $H_{298}^\circ - H_0^\circ$	6.197 6 kJ/mol

REFERENCES

[1] For extensive tabulations of the thermodynamic and physical properties of xenon, see W. Braker and A. L. Mossman, *The Matheson Unabridged Gas Data Book, 1975*, Matheson, East Rutherford, New Jersey.

[2] W. Braker, A. L. Mossman, and D. Siegel, *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd edition, *1977*, pp. 55–57, Matheson, Lyndhurst, New Jersey.

[3] B. J. Zwolinski, *et al.*, *Selected Values of Chemical Compounds, 1968*, Volume 1, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

[4] A. C. H. Hallett in *Argon, Helium and the Rare Gases*, G. A. Cook editor, *1961*, Volume 1, p. 328, Interscience Publishers, Inc., New York, New York.

[5] **Ibid.**, p. 293.

[6] **Ibid.**, pp. 302–303.

[7] R. C. Reid and T. °K. Sherwood, *The Properties of Gases and Liquids*, 2nd edition, *1966*, pp. 587–595, McGraw-Hill Book Co., Inc., New York, New York.

Table 1. THERMODYNAMIC PROPERTIES OF REAL GAS XENON (6)

ENTHALPY DIFFERENCE, **H** (H_T-H°_0), J/mol; ENTROPY, **S**, J/(mol·°K); FREE ENERGY, **F** (F_T-H°_0), J/mol

REFERENCE STATE FOR H, S, AND F: 273.15 °K (0 °C) AND 101.325 kPa (1 atm)

Pressure kPa	atm		Temperature, °K 273.15	298.15	323.15	373.15	423.15
101.325	1	H	0.00	526.14	1 051.0	2 097 8	3 142.4
		S	0.00	1.845	3.535	6.548	9.171
		F	0.00	−24.3	−91.6	−345.6	−738.5
5 066.250	50	H		−2 220 4	−1 022.6	657.7	2 044.3
		S		−37.447	−33.568	−28.711	−25.221
		F		8 944.1	9 824.9	11 371	12 716
10 132.500	100	H		−7 719.1	−4 918.7	−1 117.5	837.6
		S		−58.141	−49.133	−38.033	−33.104
		F		9 614.4	10 959	13 074	14 846
20 265.000	200	H		−8 268.4	−6 948.0	−3 969.4	−1 330.5
		S		−62.233	−57.957	−49.384	−42.731
		F		10 286	11 781	14 458	16 751
40 530.000	400	H		−8 170.1	−7 140.0	−4 979.4	−2 890.7
		S		−65.844	−62.505	−56.279	−51.020
		F		11.461	13 058	16 021	18 698
81 060.000	800	H		−7 254.2	−6 348.8	−4 482.7	−2 729.6
		S		−69.827	−66.890	−61.513	−57.095
		F		13 565	115 267	18 471	21 430
121 590	1 200	H		−6 102.8	−5 237.5	−3 456.0	−1 801.2
		S		−72.479	−69.672	−64.534	−60.367
		F		15 507	17 277	20 625	23 743
162 120	1 600	H		−4 876.9	−4 029.2	−2 282.8	−672.8
		S		−74.546	−71.802	−66.760	−62.706
		F		17 349	19 174	22 629	25 861
202 650	2 000	H		−3 617.1	−2 780.7	−1 050.6	536.8
		S		−76.270	−73.559	−68.559	−64.567
		F		19 123	20 990	24 532	27 859

Table 2. COMPRESSIBILITY FACTORS FOR XENON (Z = PV/RT) (7)

Temperature, °K	Pressure; kPa 101.325	1 013.25	2 026.50	3 039.75	4 053.00	5 066.25
273.15	0.975	0.937	0.832	0.734	—	—
298.15	0.975	0.948	0.889	0.823	0.748	0.658
323.15	0.985	0.963	0.918	0.873	0.824	0.769
373.15	0.991	0.978	0.955	0.927	0.908	0.880
423.15	0.994	0.988	0.977	0.962	0.950	0.941

APPENDIX I

GENERAL PRECAUTIONS IN HANDLING AND STORAGE

1. Never drop cylinders or permit them to strike each other violently.
2. Cylinders should be assigned a definite area for storage. The area should be dry, cool, well-ventilated, and preferably fire-resistant. Keep cylinders protected from excessive temperature rise by storing them away from radiators or other sources of heat. Storage conditions should comply with local, state and federal regulations.
3. Cylinders may be stored in the open, but in such cases should be protected against extremes of weather and from the dampness of the ground to prevent rusting. During the summer, cylinders stored in the open should be shaded against the continuous direct rays of the sun in those localities where extreme temperatures prevail.
4. The valve protection cap should be left in place until the cylinder has been secured against a wall or bench, or placed in a cylinder stand, and is ready to be used.
5. Avoid dragging, rolling, or sliding cylinders, even for a short distance. They should be moved by means of a suitable hand truck.
6. Never tamper with safety devices in valves or cylinders.
7. When returning empty cylinders, close the valve before shipment, leaving some positive pressure in the cylinder. Mark or label the cylinder EMPTY. Do not store full and empty cylinders together.
8. No part of a cylinder should be subjected to a temperature higher than 125°F. A flame should never be permitted to come in contact with any part of a compressed gas cylinder. Temperatures in excess of 125°F may cause a cylinder to become liquid full and create dangerous hydrostatic pressures.
9. Cylinder content of liquefied gases is determined by weight; the cylinder content of nonliquefied gases by gauge pressure.
10. Before using, read all data sheets and label information associated with the use of the gas concerned.

GENERAL PRECAUTIONS IN USING GASES

1. Close off main cylinder valve when not in use.
2. Needle valve or auxiliary cut off valve in the line and located at the cylinder. Do not rely purely on the cylinder valve.
3. Turnover cylinders in reasonable time. Corrosive gases should be three months or less.
4. Always use gases in areas where adequate ventilation is provided.
5. Keep cylinders in outside storage, or have manifold piping low pressure gas into buildings.
6. Use the smallest practical size of cylinder for your gas applications.

APPENDIX II

DISPOSAL OF LEAKING CYLINDERS

On occasion, despite precautions, gas cylinders or systems may develop leaks. We recommend that the supplier be contacted to determine appropriate disposal procedures. Disposal procedures described below should be investigated as to their conformity with all regulations issued by the appropriate authorities. Disposal of gases is a complex problem and should be undertaken only by personnel who are familiar with the gas involved and the disposal procedures. When in doubt, contact the supplier for instructions.

If in doubt as to the proper disposal procedures, isolate the leaking cylinder in a vented or open area, and contact the supplier for disposal procedures.

A-FLAMMABLE GASES

Leaks of flammable gases require special handling. All sources of ignition should be eliminated at once. If practical, the cylinder should be removed to a safe, out-of-doors area, and plainly tagged as defective. If the gas is also toxic (e.g., carbon monoxide), proper breathing equipment should be donned before transporting the cylinder to the disposal area. Warnings should be posted in the area to prevent persons from approaching the cylinder with lit cigarettes or open flames. Attach appropriate control valve to the cylinder valve outlet and adjust the gas discharge to a moderate discharge rate. When the cylinder is empty, close the cylinder valve and follow the supplier's directions for cylinder return, after informing the supplier of the defect.

The local fire department may be of help in removing the leaking cylinder to the disposal area.

Undoubtly, the best procedure for disposal of flammable gases would be to burn the gas if a burning unit is available in the plant.

B-ALKALINE GASES

The alkaline gases are corrosive, flammable, and toxic. Leaks of alkaline gases, such as ammonia and the lower alkyl amines, may be handled in the following manner. Shut off all ignition sources. Put on appropriate protective equipment (face mask, rubber gloves, breathing equipment) before transporting the cylinder to a hood with forced ventilation, or to a safe out-of-doors area. If leak is minor, wrap wet rags around leaking part of cylinder and transport the cylinder to the disposal area. Warnings should be posted in the area to prevent persons from approaching with lit cigarettes or open flames. Attach an appropriate control valve equipped with a trap or check valve and a long piece of flexible hose connected to the control valve outlet. Discharge the gas at a moderate rate into an adequate amount of 10–20% aqueous sulfuric acid solution. After all the gas has been discharged, the vessel containing the resulting solution may be transported to the plant treating unit for neutralization and disposal. When the cylinder is empty, close the control valve. The cylinder should be tagged as defective and returned to the supplier according to the supplier's directions.

The local fire department may be of help in transporting the leaking cylinder to the disposal area.

C-INERT GASES

Leaking cylinders of inert gases, such as argon, helium, nitrogen, etc., do not represent a hazard unless they are situated in confined places with no ventilation. In the latter case, the inert gases may create a hazard by displacing the amount of air necessary to support life. The cylinder should be removed to an out-of-doors area or a hood with forced ventilation (breathing equipment should be worn, however, if the issuing gas is in a confined place). The cylinder valve should be "cracked" to allow the gas to discharge at a moderate rate. After the gas has been discharged, close the cylinder valve. The cylinder should be tagged as defective and returned to the supplier according to the supplier's directions.

D-ACID GASES

Acid gases are corrosive and toxic. Therefore, put on appropriate protective equipment (face shield, rubber gloves, breathing equipment) before transporting the leaking cylinder to a safe out-of-doors area or a hood with forced ventilation. Attach an appropriate control valve provided with a trap or check valve and a long piece of flexible hose connected to the control valve outlet. Discharge the gas at a moderate rate into an adequate amount of about 15% aqueous sodium hydroxide or other alkali in a suitable container. When all the gas has been discharged, close the cylinder valve, and transport the resulting salt solution to the plant treating unit for neutralization and disposal. The cylinder should be tagged as defective and returned to the supplier according to the supplier's directions.