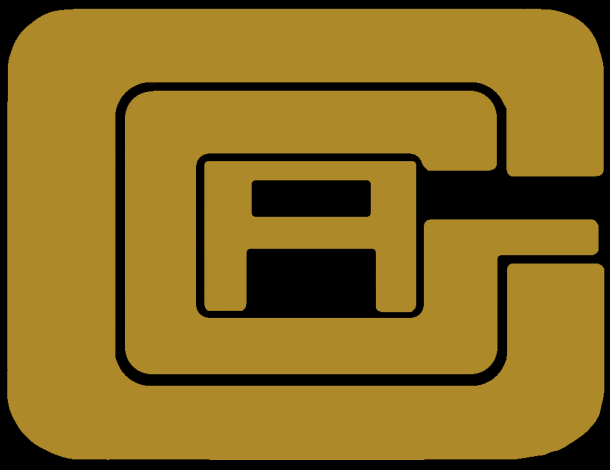
HANDBOOK OF COMPRESSED GASES

Fourth Edition

Compressed Gas Association, Inc.



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Foreword

In the field of compressed gases and related equipment, there is an expanding core of essential knowledge that people handling and using these materials should be familiar with or should know where to find.

The focus of this book concerns the properties and the accepted means of transportation, storage, and handling of compressed gases. This handbook is simultaneously intended as an overview of the subject and a source of supplementary information. It is also intended to serve as a guide to pertinent federal regulatory requirements and published standards of the Compressed Gas Association and other standards-developing organizations.

The Association advises readers that the CGA technical publications remain the official statement of policy on a particular matter. Reference is made throughout this text to the numerous technical publications published by the Compressed Gas Association. Some of these publications have been incorporated by reference into federal, state, provincial, and local regulations.

Since the CGA publications are reviewed on a periodic basis, whenever the text of this handbook conflicts with corresponding information in the CGA technical pamphlets, the most recently printed material shall take precedence.

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Preface

Industrial and medical gases continue to enjoy an expanding role throughout our economy. Almost everywhere we go we find essential and life-enhancing gases. We find oxy-acetylene torches at the muffler shop as in welding at a construction site. The portable oxygen pack provides mobility to those with respiratory problems. Self-contained breathing apparatus (SCBA) are used by fire fighters and underwater divers. The carbon dioxide containers under restaurant counters put sparkle into our soft drinks, and the less obvious refrigerant gases air condition our homes and automobiles as well as ensure the preservation of the food in our refrigerators. These are examples of some of the more common ways we use gases to enhance our lifestyle. More uses of gases are mentioned in Chapter 1 of this book.

This fourth edition of the *Handbook of Compressed Gases* comes at a time when the use of gases continues to grow rapidly as new technologies emerge. Gases known primarily as scientific curiosities a few years ago are now essential to semiconductor and other high technology manufacture.

To maintain the very fine safety record our industry has established since the turn of the century, new safety standards and procedures must accompany these new applications. New applications result in changing regulations for transportation, handling, and use of these gases. The fourth edition of the handbook is intended to keep pace with these changes.

For 85 years, the Compressed Gas Association has been dedicated to enhancing safety. The Association's mission statement describes activities that fulfill its purpose, which is:

> To develop, promote and coordinate technical, educational and standards activities in the industrial gas industry; to promote public and occupational safety; to safeguard public and private property and the environment; to interactively assist federal, state, provincial and local governments in developing responsible regulations and codes; and to cooperate with other trade and technical organizations in safety and technical matters, standards and public programs relating to the industrial gas industry.

The fourth edition of the handbook is an extension of this intent.

Millions of workers, homeowners, hobbyists, and educators handle and use gases in their daily activities. Most of those people have no technical expertise, yet they safely use potentially hazardous materials. Gases can be hazardous by virtue of pressure, flammability, oxygen deficiency, corrosivity, toxicity or other physical and chemical properties. The industrial gas industry and the Compressed Gas Association are proud that despite the range of hazards, the safety record of its products is among the best in industry.

The fourth edition of the handbook represents a thorough review and revision of the text. It is intended to provide engineers and scientists as well as those without detailed technical training and experience, a basic understanding of the properties, safety considerations, and regulatory framework regarding industrial and medical gases and related equipment. Individuals needing greater detail may find this handbook a useful guide to standards and recommended practices published by the Compressed Gas Association and other organizations.

The Association is indebted to the many volunteers who contributed generously to creating this fourth edition of the handbook. In particular, we recognize the chapter coordinators, technical editors and editors including:

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The Compressed Gas Association gratefully acknowledges E. I. Du Pont de Nemours & Co. and Matheson Gas Products, Inc. for its help in preparing vapor pressure curves for many of the gases covered in this book. Likewise, the Association is grateful to AGA Gas Inc. for permission to adapt and reprint the text in Chapter 4.

The contributors to this book have tried to provide the most accurate information available. These efforts notwithstanding, we recognize that such works are generally not without error, whether due to the difficulties of compiling complex technical data into a finished publication, or merely from the passage of time and changes in the body of technical information itself. We therefore welcome being advised of any errors detected by readers and appreciate the citation of relevant reference sources where applicable.

Carl T. Johnson, President
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Introduction

The Handbook of Compressed Gases is intended to serve the needs of a wide audience. Among others, this group will include laymen, teachers and students, workers and supervisors in many industrial sectors, scientists and engineers, and managerial personnel. The broad range of people who may have occasion to become familiar with the subject of compressed gases and compressed gas equipment is indicative of the pervasive role these materials play throughout our society. Much diversity in the amount of formal technical training will also be found within these groups. There will also be differences in the interests of readers, especially between those within the industry, who have acquired considerable familiarity with the subject over the years, and readers who may be approaching the subject for the first time.

In an attempt to satisfy the needs of all such readers, this handbook has been divided into three parts. The contents of each part will be briefly described in the Part Introductions. By structuring the book in this way, the contributors hope to enable readers to better focus on a particular area and level of interest. Bracketed numbers within the text indicates references to regulations, standards, and other citations. These references are listed in accordance with their order of appearance at the end of each chapter or gas monograph.

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PART I

Compressed Gases and Related Equipment

Part I presents basic information concerning compressed gases and cryogenic liquids and related equipment. Introductory presentations give an overview of the uses for these gases, the regulatory framework involved in their shipping and handling, the scientific basis for understanding the behavior of gases, the types of containers used to contain these materials, and basic guidelines for their safe handling.

The Compressed Gas Association, Inc. (CGA) issues general industry standards and recommendations for compressed gases along with a number of publications, which are concerned with highly specialized aspects of the industry. Reference to these standards and recommendations, as well as those of other organizations, is made throughout the chapters of Parts I and in the individual gas monographs in Part II. A full descriptive listing of CGA publications and audiovisuals appears as an appendix in Part III.

A brief explanation of the International System of Units (SI) and some of the conversion factors used in this book can be found in the Units of Measure section at the end of Chapter 1. The appendices in Part III include more extensive information on technical abbreviations, acronyms and conversion factors.

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CHAPTER 1

Compressed Gases Today

INTRODUCTION

This chapter provides an introduction to compressed gases. Included are descriptions of the various groupings and families into which gases are categorized, as well as information concerning standard units of measurement. This is useful background information especially to anyone unfamiliar with gases.

Since this handbook provides information for the general reader, as well as the professional, it does not fully reproduce published standards for procedures, equipment, design, etc. It does, however, present the essential content of some standards and clear references if more detailed information is required. CGA recommends using the most current editions of standards, specifications and all reference documents unless otherwise specified in regulations. For a current publications catalog contact CGA.

Modern Uses of Compressed Gases

Compressed gases have become so widely used in modern society that we often take them for granted. Yet without them, civilized life as we know it would simply not be possible.

Compressed gases have enabled humans to venture deep below the seas and travel far into space. Gases provide the tremendous power needed to launch spacecraft, as well as the micro-thrusts needed to control and maneuver space vehicles. (See Fig. 1-1.)

High technology applications of compressed gases have been instrumental in producing many new benefits including computers whose integrated semiconductor circuits can be produced only in high purity inert gas atmospheres with special gases that are used in the manufacture of components with small dimensions.

Medical techniques involving special gas mixtures such as those required in hyperbaric chambers and other oxygen therapies have achieved remarkable results. Magnetic Resonance Imaging (MRI), which is used for diagnostic purposes, and special low-temperature surgical procedures, known as cryosurgery, also require the use of compressed gases. (See Fig. 1-2.)

The fields of refrigeration, air conditioning, metalworking, medicine, food processing, plastics production, vehicular travel, and aerosol packaging are just a few of the other technologies that depend to some extent on compressed gases. In short, the use of compressed gases is an essential part of modern life.

Further discussion of the uses of specific gases is given in the remainder of this chapter and in the gas monographs in Part II. The physical world inhabited by mankind largely consists of three states of matter – solid, liquid, and gas. Suffice it to say that the history of gas use is the history of how humans have used compressed gases for the improvement of life.

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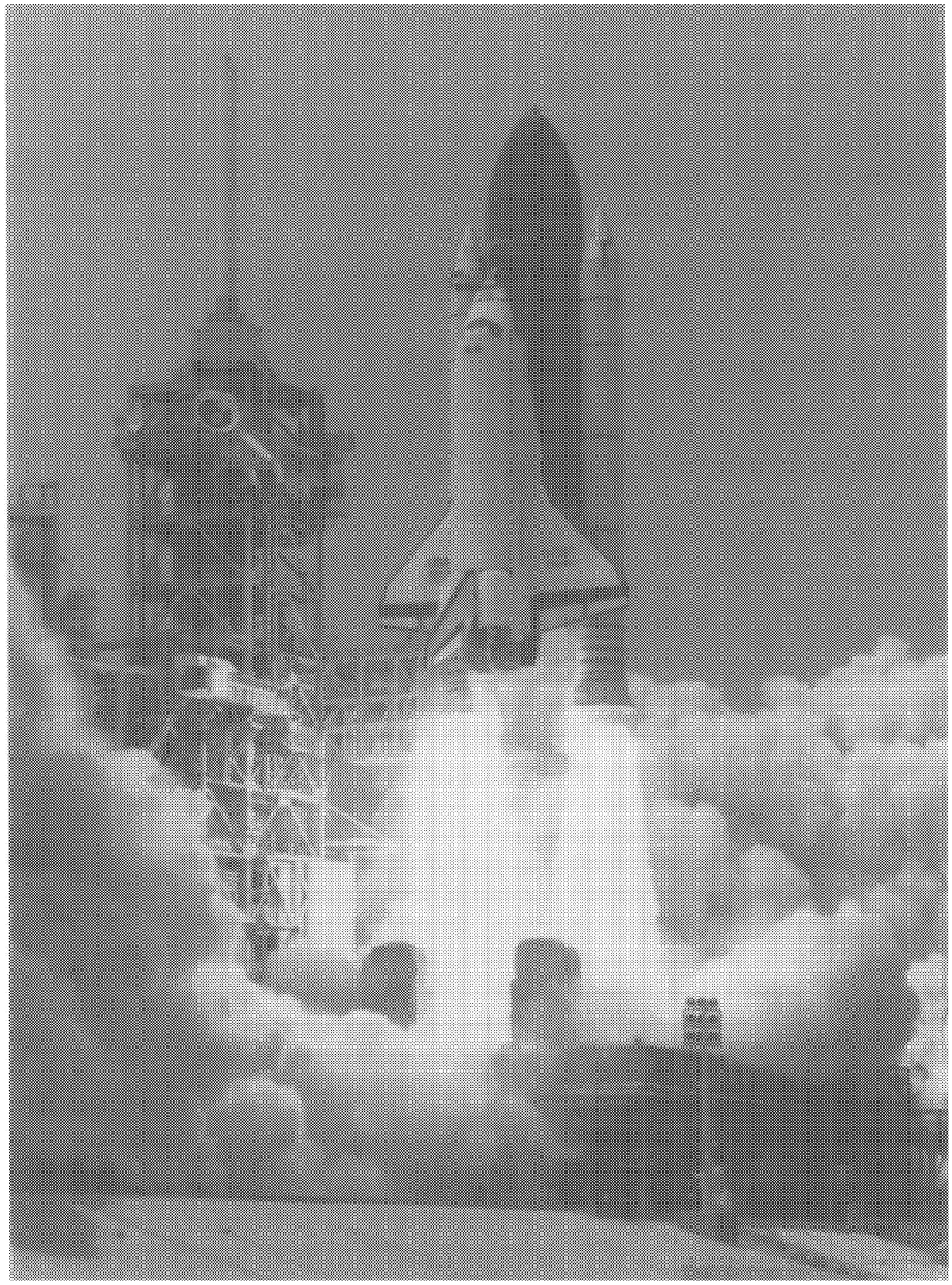

Fig. 1-1. The NASA Space Shuttle Program represents one of the more dramatic applications for compressed gases. (Photo courtesy of NASA.)

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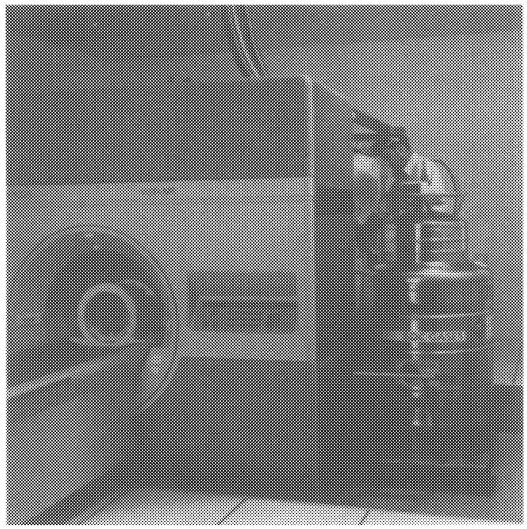

Fig. 1-2. Compressed gases in medical service include cryogenic liquids for operating superconducting magnets during magnetic resonance imaging (MRI).

What Are Gases?

Gases are any substances that boil at atmospheric pressure and any temperature between absolute zero, –459.67°F (–273.15°C), and 68°F (20°C). Eleven of the known chemical elements have boiling points within this range. These elements are hydrogen, nitrogen, oxygen, fluorine, chlorine, helium, neon, argon, krypton, xenon, and radon. In addition to chemical elements that exist as gases, there are many gases that are chemical compounds such as ammonia, sulfur dioxide, and silane. Furthermore, gases may be mixed together to form an unlimited number of mixtures, air being the most common.

What is a "Compressed Gas"?

Currently there are more than 200 different substances commonly shipped in compressed gas containers that can be considered compressed gases. The Department of Transportation (DOT) defines these materials based on their properties such as vapor pressure, flammability, toxicity, and physical state in the container. The specific definitions in this handbook according to DOT classification are in three Class 2 compressed gas divisions: 2.1 (flammable gas), 2.2 (nonflammable compressed gas), 2.3 (gas poisonous by inhalation) [1].

More specific definitions based upon hazard class may be found in current regulations of DOT and Transport Canada (TC) [1, 2].

TABLE 1-1. BOILING POINTS OF SOME TYPICAL NONLIQUEFIED GASES.[a]

Oxygen	Helium	Nitrogen
–297°F –183°C	–452°F –269°C	–320°F –196°C

[a] At one atmosphere.

Nonliquefied and Liquefied Gases

Compressed gases may be divided into two major groups depending on their physical state in containers under certain pressures and temperatures, and their range of boiling points. These groups are denoted as nonliquefied gases and liquefied gases.

Nonliquefied gases are those that do not liquefy at ordinary ambient temperatures regardless of the pressure applied. Nonliquefied gases are elements or compounds that have relatively low boiling points, typically –130°F (–90°C) and lower. (See Table 1-1.) Of course, these gases do become liquids if cooled to temperatures below their boiling points. When these gases become liquefied at these very low temperatures, they are referred to as cryogenic liquids.

Oxygen, helium, and nitrogen are examples of nonliquefied gases in wide use as compressed gases and cryogenic liquids. Note that the lower limit for cryogenic temperatures is fixed by absolute zero, –459.67°F (–273.15°C). The upper limit is defined by DOT to be –130°F (–90°C) at 101.3 kPa [1].

Charging pressures for these nonliquefied gases can be more than 2000 psig (13 790 kPa) at 70°F (21.1°C). However, when cooled to cryogenic temperatures near their boiling points, nonliquefied gases will have low charging pressures. Typical storage vessels will have design pressures up to about 250 psig (1720 kPa) to allow for a rise in pressure with ambient heating.

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TABLE 1-2. BOILING POINT AND PRESSURES OF SOME TYPICAL LIQUEFIED GASES AT 70°F.

Ammonia[a]	Chlorine[b]	Propane[c]	Carbon Dioxide[d]
–28°F	– 29°F	–44°F	–109°F (sublimes to gas)
–33.3°C	–33.9°C	–42.2°C	–78.3°C

[a] The pressure of ammonia at 70°F (21.1°C) is 114.1 psig (790 kPa)

[b] The pressure of chlorine at 70°F (21.1°C) is 85.5 psig (590 kPa)

[c] The pressure of propane at 70°F (21.1°C) is 109.7 psig (760 kPa)

[d] The pressure of carbon dioxide at 70°F (21.1°C) is 838 psig (5780 kPa)

Liquefied gases are those that generally become liquids in containers at ambient temperatures and at pressures from 25 psig to 1500 psig (172 kPa to 10 340 kPa). (See Table 1-2.) Liquefied gases are elements or compounds that have boiling points relatively near atmospheric temperatures. These range from –130°F to 68°F (–90°C to 20°C). Such liquefied gases solidify at cryogenic temperatures. Of these, only carbon dioxide has come into commercial use in solid form as "dry ice."

Liquefied gases are shipped under rules that limit the maximum amount that can be put into a container to allow space for liquid expansion with rising temperatures.

A third grouping is dissolved gas. Acetylene is the only widely used gas in this category. The acetylene gas is dissolved in acetone or dimethylformamide (DMF) that is absorbed into small cells of porous material that fills the inside of an acetylene cylinder. By storing the acetylene dissolved in acetone or DMF, it is possible to ship it at settled pressures of 250 psig (1720 kPa) at 70°F (21.1°C). If gaseous acetylene is stored in a typical gas cylinder shell at shipping pressure without porous mass and acetone, it can decompose with explosive violence upon sufficient thermal energy input. Use of acetylene in transmission piping, hoses, etc. is limited to 15 psig (103 kPa) maximum pressure in North America. The presence of the porous filler material in acetylene cylinders renders them unique in design and unsuitable for use with other gases.

Besides its wide use as a fuel gas, acetylene is used in a number of chemical processes. Some consumers of bulk acetylene and most industrial suppliers produce acetylene directly by the reaction of calcium carbide and water.

FAMILIES OF COMPRESSED GASES

Compressed gases are often described according to loosely knit families. Such designations can be somewhat arbitrary and are usually based on a common source, a similar use, or a related chemical structure.

Classification of gases by families can sometimes be misleading because individual gases may often be used in a number of very different ways. Nitrous oxide, for example, belongs to several families—it is a prominent member of the medical gases family, is used as a propellant gas, and also is used as a refrigerant gas.

Similarly, oxygen has a large and growing application in medicine where it is used alone, as well as mixed with carbon dioxide, nitrogen, or helium for many kinds of respiratory therapy. Oxygen is also used in welding and steel making.

Part II of this book provides monographs on individual gases and indicates predominant chemical characteristics for each gas. However, it is important to remember that any particular gas may exhibit several characteristics to varying extents. The following paragraphs describe some typical families by which compressed gases may be categorized.

Atmospheric Gases

Atmospheric gases are one of the largest families of compressed gases. The most plentiful member of this family is nitrogen, constituting 78 percent of the atmospheric air by volume. The second most abundant member is oxygen, which constitutes 21 percent of the atmosphere. Nitrogen is a basic constituent of amino acids, which serve as the building blocks of proteins in all living organisms. Oxygen is essential to animal life by virtue of its role in metabolic respiration.

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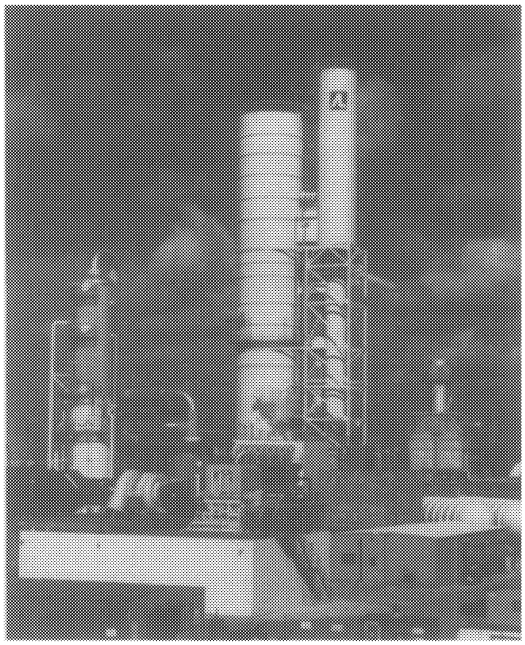

Fig. 1-3. A modern air separation plant liquefies gases from the atmosphere and extracts the constituents through fractional distillation.

But these two gases have a great many other uses as well. Oxygen is used to produce stronger steels less expensively. It is also used together with acetylene and other fuel gases such as propane to weld or cut steel in fabricating structures and machinery. It is used in medical treatment and respiratory therapy, to name two prominent applications. Liquid nitrogen is used as a refrigerant for the transportation of perishable goods and in the quick-freezing of fruits and vegetables. Gaseous nitrogen is often used as an inerting or purging medium.

Most of the remaining 1 percent of the atmosphere consists of gases sharing the property of chemical inertness. These gases include argon, along with minute amounts of helium, neon, krypton, xenon, and radon. The last four are frequently called the "rare gases" due to their scarcity. Argon, helium, krypton, and neon are used to obtain the glowing colored messages we see in the so-called neon signs. Inert gas atmospheres provided by argon or helium are also essential to the welding of stainless steels and special metals like titanium and zirconium.

Hydrogen also occurs minutely in the atmosphere along with large amounts of water vapor, small amounts of carbon dioxide, and a variety of other trace constituents.

Commercial Production of Atmospheric Gases

The production of large scale quantities of the more abundant atmospheric gases and the rare gases is accomplished by cryogenic fractional distillation of atmospheric air. The general techniques required to liquefy and distill atmospheric air were known and applied at the beginning of the twentieth century.

The introduction of the Linde single-column system in 1902, which cryogenically rectified air for oxygen revolutionized the production of oxygen and ushered in a new industry. In 1910, the double-column system was introduced. The double-column innovation fixed the fundamental pattern for all successive cryogenic fractional distillation processes used to produce oxygen, nitrogen, and argon from atmospheric air. (See Fig. 1-3.)

Compressed atmospheric air, cleansed of atmospheric contaminants, is first cooled to near its liquefaction temperature before being distilled into its principal components. The air is progressively cooled in a heat exchanger against the colder products of the fractional distillation process, followed by expansion. The expansion process may take place in a throttling valve, which can decrease temperature, in an expansion engine, which decreases both temperature and enthalpy, or in a combination of both processes. Next, the cold air enters the double column (two distillation columns interconnected by a common condenser-reboiler heat exchanger) where the process of rectification begins. The air is liquefied and fractionally distilled to obtain separate nitrogen and oxygen-rich liquids in the pressure column section of the double column. The products of this operation are transferred to the upper column section of the double column where the final distillation process takes place to produce high purity oxygen, nitrogen, and an argon-rich oxygen stream.

The quantity and quality of oxygen and nitrogen products, both gaseous and liquid, withdrawn from the distillation process, depend on the design criteria applied. Oxygen has always

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been the desired product, and the drive to improve the technology to obtain it cryogenically continues today. Oxygen purities as high as 99.99 percent pure are achievable, with the recovery of oxygen from the distilled air now approaching 100 percent. The demand by industry for more and higher purity nitrogen has forced the development of new technologies to improve cryogenic nitrogen production. The widespread use of molecular sieves to purify air of its atmospheric contaminants has allowed the cryogenic distillation process to produce more nitrogen. (See Fig. 1-4.)

Two separate cryogenic fractional distillation process steps are required to produce refined argon. The first step involves the removal of most of the oxygen from the argon-rich oxygen stream produced from the distillation process in the upper column of the double column. The second step involves the removal of the nitrogen impurity from the argon. The first step is accomplished in a crude argon distillation column, which is normally integral to the operation of the upper column. An assay of the argon vapor leaving the crude argon distillation column ranges between 97 percent and 99 percent pure argon, depending on the efficiency of the column and the state of the technology used. The oxygen component in the crude argon stream, now at ambient temperature, can be removed by combining catalytically with hydrogen to form water vapor. The water vapor produced is removed and the argon stream, composed mostly of argon and small amounts of nitrogen and hydrogen impurities, is recooled to near its liquid point temperature. Recent technological developments have markedly improved the efficiency of the crude argon distillation column to remove the oxygen impurity from the crude argon, thus eliminating the need for the catalytic combustion furnace and associated equipment.

The pure argon distillation column completes the refining process, yielding a high purity argon liquid. The principal purpose of the pure column is to remove nitrogen and hydrogen impurities from the argon stream. Today, it is technically possible and economically desirable to recover up to 90 percent of all the available argon in the atmospheric air compressed into the air separation plant. An assay of refined liquid argon will typically measure a purity of 99.999 percent pure argon.

The cryogenic fractional distillation of large quantities of atmospheric air is the only practical means available for acquiring the rare gases krypton, neon, and xenon. The recovery of crude rare gases is accomplished in multiple cryogenic fractional distillation columns and

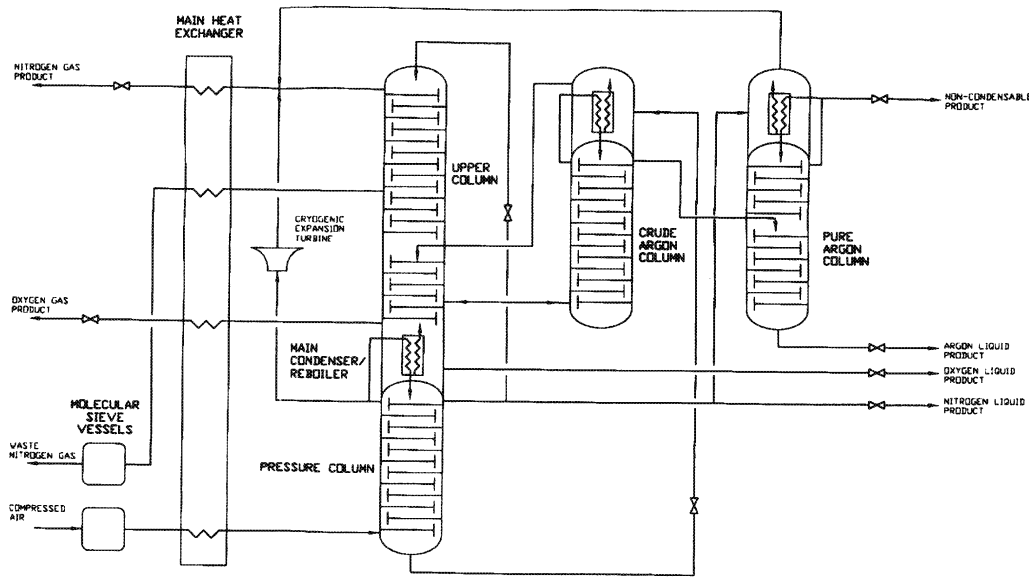

Fig. 1-4. Diagram of a cryogenic fractional distillation process using molecular sieve to purify the air stream, a double-column system to extract oxygen and nitrogen, and a cryo-argon process to refine argon.

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purification systems associated with and obtaining their feed stock from a double-column operation. Final refining of the recovered crude rare gases to very high purity must be accomplished in specially equipped laboratories.

More recently, processes operating at around ambient temperature have been introduced for producing nitrogen and oxygen. These systems use the technologies of pressure swing adsorption (PSA) or membrane to affect the separation of air. These units range in size from tabletop generators to full-sized units capable of providing industrial quantities of the required gas.

Fuel Gases

Gases that burn using air or oxygen to produce heat make up a family of gases related through their major use. Its members are notably the hydrocarbon gases and liquefied petroleum gases (LP-gases) such as propane and butane. Methane, the largest component of natural gas, is another representative of the family, and welding gases such as acetylene are somewhat special representatives. (See Fig. 1-5.) Liquefied petroleum gases are widely used as portable fuel where pipeline natural gas is not available. Some other gases in the fuel gas family are the inhibited methylacetylene- propadiene mixtures that resemble LP-gas in many ways.

Liquefied methane, also referred to as liquefied natural gas (LNG), is used for heating in the electric utility industry. Electric power plants liquefy the gas from pipelines over a long period and use the gas when electric usage peaks (peak shaving). LNG and compressed natural gas (CNG) are increasingly used in alternate fueled vehicles.

Refrigerant Gases

Another family is the refrigerant gases. Gases that liquefy easily under pressure are used as refrigerant gases. In this liquid state, refrigerant gases absorb large amounts of heat as they are vaporized into gas in the cooling coils of refrigeration equipment. Any liquefied gas is a strong candidate for inclusion in the refrigerant family, and even some gases more commonly used in other ways such as methane have been classified as refrigerant gases by the American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE). While not refrigerant gases in the mechanical sense, due to their extremely low temperatures, cryogenic liquids such as liquid nitrogen also find use in food preservation and processing. (See Fig. 1-6.)

Among the refrigerant gases, the halogenated hydrocarbons (halocarbons) are the most popular. This family is very large since there are many combinations by which volatile hydrocarbons can be halogenated. Halogenated hydrocarbons serve well as refrigerant gases because most of them are chemically inert to a large extent, and they can be selected, mixed, and compounded to provide physical properties desired for particular refrigerant applications. Due to recognized harmful effects of certain halogenated hydrocarbons on the earth's environment (global warming, ozone depletion, etc.), they are being phased out of production.

Dry or anhydrous ammonia liquefies under low pressure and was the earliest widely used refrigerant gas and is still used for this purpose, usually in larger refrigeration operations.

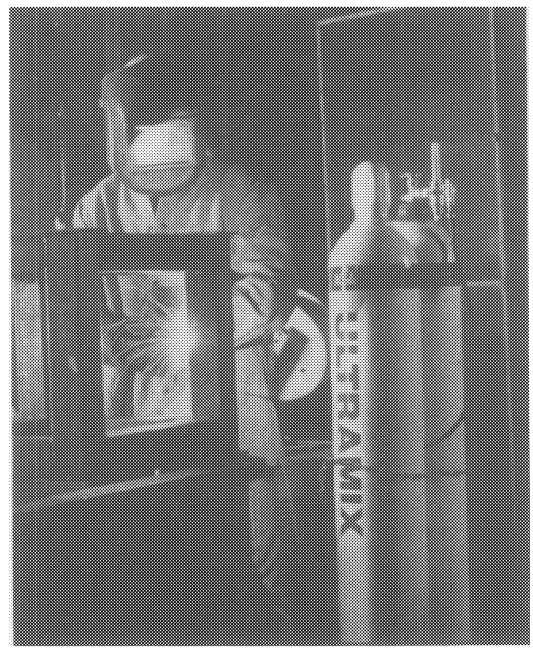

Fig. 1-5. Modern welding techniques use compressed gases in numerous ways.

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Fig. 1-6. Compressed gases find wide use in the processing, preservation, and preparation of foods. The cryofreeze process utilizes liquid nitrogen to quick-freeze hamburger patties.

Poison Gases

Gases that have LC_{50} values of 5000 ppm or less and are recognized by DOT and TC as poison gases are considered in North America to be the poison gas family. These gases are further classified into one of four subsidiary categories with LC_{50} breakpoints of 200, 2000, and 3000 ppm. The toxicity is inversely proportional to the magnitude of the LC_{50} value. These poison gases find uses in both the semiconductor, as well as the chemical process industries. An example of the former is arsine (LC_{50} = 20 ppm), which is used in the production of advanced semiconductor materials. (See Fig.1-7.) An example in the chemical process industry is hydrogen sulfide (LC_{50} = 712 ppm), which is used as a chemical intermediate.

Poison gases with an LC_{50} that is less than 200 ppm are listed by DOT as "Poison Gas, Hazard Zone A" and "extremely poisonous by inhalation." Special packaging requirements are enumerated by DOT for these gases. Specific information on the safe handling of gases of this type is provided in the individual gas monographs.

Gases with no Family Ties

Other gases that are important commercially have no marked family ties. For example, the methylamines serve as chemical intermediate sources of reactive organic nitrogen, and methyl mercaptan helps in the synthesis of insecticides. The mercaptans are also used in odorizing natural gas to allow easy leak detection.

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Fig. 1-7. The use of compressed gases in the manufacture of semiconductors for the electronics industry has become a major application. Here, a portable "clean room" and advanced pipe welding techniques are used to ensure highest possible gas purity.

Sulfur dioxide is a liquefied gas used widely as a preservative and bleach in processing foods, as well as bleach in manufacturing sulfite papers and artificial silk. It is also used as an additive to irrigating water to improve alkaline soils in the American Southwest.

Carbon monoxide is used to make other chemicals including the urethane plastics. It is also used in some metallurgical processes—one for refining high purity nickel, and another, in conjunction with chlorine and nitrogen, for removing some gases from molten aluminum. Mixtures containing small amounts of carbon monoxide are used for medical pulmonary function testing.

Fluorine is used to make sulfur hexafluoride, a gas with high dielectric strength used in electrical equipment; and nitrogen trifluoride, a gas used in the microelectronics industry for cleaning, etching, and deposition applications. Anhydrous ammonia is used to fertilize croplands, resulting in higher yields at lower cost. Nitrous oxide and other anesthetic gases are needed in modern surgery. Acetylene, 1,3-butadiene, carbon monoxide, chlorine, the methylamines, and vinyl chloride make possible the production of plastics, synthetic rubber, and pharmaceuticals. Nitrous oxide and carbon dioxide are used as propellants for edible products such as whipped dessert toppings. Other products such as perfumes, shampoos, shaving lathers, paints, and insecticides are pressurized with gases such as butane, an LP-gas. Chlorine is used in swimming pools and in the treatment of drinking water.

Some high purity helium is obtained through air liquefaction and fractionation, but most helium obtained today comes from natural gas wells. Helium is used as a carrier gas in a variety of analytical instruments and as a shielding gas. Liquid helium is used as a coolant for superconductivity magnets and other devices.

Carbon dioxide fire extinguishers are commonly used for protection against chemical and electrical fires, while carbon dioxide dissolved under pressure makes the sparkle in "carbonated" beverages. Solid carbon dioxide, commonly called dry ice, has largely replaced water ice in the handling of some perishable foods where mechanical refrigeration is unavailable.

Specialty gases are another important and growing segment of the compressed gas industry. The semiconductor manufacturing industry uses specialty gases such as silane in very pure form to manufacture the microchips that are the "brains" of all sizes of computers.

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SAFETY PROGRAMS

Due to the potential hazards resulting from the inherent stored energy, chemical reactivity, and possible biological effects of compressed gases, the necessity for sound safety practices in their storage, transportation, handling, and use is a primary concern of the industry.

Emergency Response

Chemical Emergency Transportation Center (CHEMTREC), the emergency response agency of the Chemical Manufacturers Association (CMA), assists local authorities in handling transportation emergencies involving chemicals, including compressed gases. Their work has had a significant impact on reducing the potential damage from such emergencies. CGA has cooperated in this work and endeavored to expand its effectiveness by instituting its own Compressed Gas Emergency Action Plan (COMPGEAP®) to work in conjunction with CHEMTREC. In Canada, members of CGA Canada have organized COMPGEAP Canada, using their Emergency Response Assistance Plans (ERAP), developed as required by the *Transportation of Dangerous Goods* (TDG) *Regulations*, to provide a mutual assistance plan covering the country. More discussion of emergency response plans will be found in Chapter 2.

A Glance at Safety Hazards

Practically all gases can act as simple asphyxiants by displacing the natural oxygen in the air. The chief precaution against this potential hazard is adequate ventilation of all enclosed areas in which unsafe concentrations may build up. It is imperative to avoid entering unventilated areas that may contain high concentrations of gases other than air without first using a self-contained or hose-line air supply.

Some gases can also have a toxic effect on the human system either by being inhaled or by having high vapor concentrations of liquefied gas come in contact with the skin or eyes. Precautions against liquefied gases and cryogenic liquids that are toxic or very cold, or both, include thorough knowledge and training for all personnel handling such gases, and the development of foolproof procedures and equipment for handling them in both normal and emergency situations.

With flammable gases, it is necessary to guard against the possibility of fire or explosion. Prime precautions against these hazards are ventilation along with procedures and equipment to detect leaks. Potential sources of ignition are to be avoided. Should a fire break out, suitable fire extinguishing apparatus and special preparations can help limit damage. For example, extinguishing a gas fire without first controlling the flammable gas source can create explosive conditions.

Oxygen poses a combustion hazard of a special kind. Although it does not itself ignite, it lowers the ignition point of flammable substances and greatly accelerates combustion. It is important to note that grease and oil are common materials that must not come in contact with oxygen and oxygen equipment.

Hazards pertaining to the possible rupture of a cylinder or other vessel containing gas at high pressure can be avoided by careful handling at all times. This includes securing cylinders to keep them from falling over, avoiding situations where a cylinder valve may be broken off, and never using compressed gas cylinders as rollers or for any other purpose other than to contain gas.

Chapter 2 provides a more thorough discussion of safety guidelines, as do other sections of this book. CGA publishes numerous industry standards and recommendations that are referred to throughout this text and are listed and briefly described in Part III, Appendix 6.

UNITS OF MEASURE

The specific types of metric units used in this book to designate metric equivalents of quantitative values given in U.S. units are SI units (International System of Units). (See Table 1-3 and Appendix 4.)

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The SI units have been adopted as an American National Standard by the American National Standards Institute (ANSI) in a booklet designated ANSI-IEEE Std. SI 10–1997, *International System of Units (SI): The Modern Metric System* [4]. The SI units were adopted by Canada in the *Weights and Measures Act of 1971* and published as a national standard in CAN/CSA Z234.1-89, *Canadian Metric Practice Guide* [5].

The SI system represents the modern version of the metric system and is an attempt to standardize systems of measurement used by different countries throughout the world. The use of SI units for metric applications has also been approved by the National Institute of Standards and Technology (NIST), the American Society for Testing and Materials (ASTM), the American Society of Mechanical Engineers (ASME), the Canadian Standards Association (CSA), the International Organization for Standardization (ISO), and other organizations.

SI units are currently divided into three classes

- base units,
- derived units, and
- supplementary units,

which together form what is called "the coherent system of SI units." The SI also includes prefixes to form decimal multiples and submultiples of SI units.

Table 1-4 gives the seven basic quantities assumed to be mutually independent, on which the SI is founded; and the names of the respective units, called SI base units.

Derived units are expressed algebraically in terms of base units or other derived units. The symbols for derived units are obtained by means of mathematical operations of multiplication

TABLE 1-3. CONVERSION FACTORS PERTINENT TO COMPRESSED GASES. U.S. UNITS TO SI UNITS

Category	U.S. Unit	Multiplied by	SI Unit
Pressure[a]	lb/in^2 (psi)	6.894 757	kPa
Pressure[a]	kg/cm^2	$9.806\ 65 \times 10^{1}$	kPa
Pressure[a]	atm	$1.013\ 25 \times 10^{2}$	kPa
Temperature[b]	°F	(°F – 32)/1.8	°C
Density	lb/ft^3	$1.601\ 846 \times 10^{1}$	kg/m^3
Volume[c,d]	ft^3	$2.831\ 685 \times 10^{-2}$	m^3
Specific volume	ft^3/lb	$6.242\ 796 \times 10^{-2}$	m^3/kg
Heat	Btu/lb	2.326	kJ/kg
Heat	Btu/ft^3	$3.725\ 895 \times 10^{1}$	kJ/m^3
Heat	Btu/gal	$2.787\ 163 \times 10^{2}$	kJ/m^3
Specific heat	Btu/(lb)(°F)	4.1868	kJ/(kg)(°C)
Weight	lb	$4.535\ 924 \times 10^{-1}$	kg (unit mass)
Length	inch	2.54×10^{-2}	m

[a] Unless otherwise stated, gauge pressure is indicated by the abbreviations *psig* whereas absolute pressure is indicated by the abbreviations *psia*. kPa shall indicate gauge pressure unless otherwise noted, as (kPa, abs) for absolute pressure and (kPa, differential) for differential pressure. All kPa values are rounded off per CGA P-11, *Metric Practice Guide for the Compressed Gas Industry* [3].

[b] The recommended SI unit of temperature is the degree Kelvin (K). However, degree Celsius (°C) values are acceptable for commonly used temperature measurements. A 1 degree difference on the Celsius scale is the same as degree difference on the Kelvin scale; 0 K equals –273.15°C.

[c] In the United States, a standard cubic foot for industrial gas use is defined at 70°F (21.1°C) and 14.696 psia (101.325 kPa, abs).

[d] In Canada, a standard cubic metre for industrial gas use is defined at 15°C (59°F) and 101.325 kPa, abs (14.696 psia). To convert cu ft at 70°F to m^3 at 15°C multiply by 0.027 728 78.

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TABLE 1-4. SI BASE UNITS.

Base quantity	SI Base Unit	
	Name	Symbol
length	meter	m
mass	kilogram	Kg
time	second	s
electric current	ampere	A
thermodynamic temperature	kelvin	K
amount of substance	mole	mol
luminous intensity	candela	cd

TABLE 1-5. SI DERIVED UNITS

	Name	Symbol
area	square meter	m^2
volume	cubic meter	m^3
speed, velocity	meter per second	m/s
acceleration	meter per second squared	m/s^2
mass density (density)	kilogram per cubic meter	kg/m^3
specific volumes	cubic meter per kilogram	m^3/kg

and division. For example, the derived unit for derived quantity molar mass (mass divided by amount of substance) is kilogram per mole, symbol kg/mol. Additional examples of derived units expressed in terms of SI base units are given in Table 1-5.

Certain SI derived units have special names and symbols; these are given in Table 1-6

Table 1-7 gives the SI prefixes that are used to form decimal multiples and submultiples of SI units. They allow very large and very small numerical values to be avoided. A prefix is attached directly to the name of the unit, and a prefix symbol attaches directly to the symbol for the unit.

Units that are outside of the SI may be divided into three categories

- those units that are accepted for use with SI,
- those units that are temporarily accepted for use with the SI, and
- those units that are not accepted for use with the SI.

Typical accepted units are time (minute, hour, day) plane angles (degree, minute, second), liter and metric ton. Two temporary units of interest to the compressed gas industry are the angstrom and the bar. Some units that are considered unacceptable are torr, standard atmosphere (atm), micron and calorie.

REFERENCES

[1] *Code of Federal Regulations*, Title 49 CFR Part 173.115 (Transportation), Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

[2] *Transportation of Dangerous Goods Regulations*, Canadian Government Publishing Centre, Supply and Services Canada, Ottawa, Ontario, Canada K1A OS9.

[3] CGA P-11, *Metric Practice Guide for the Compressed Gas Industry*, 1st ed., Compressed Gas Association, Inc., 1725 Jefferson Davis Highway, Arlington, VA 22202.

[4] ANSI-IEEE Std. SI 10–1997, *International System of Units (SI): The Modern Metric System*, 1997, Institute of Electrical and Electronics Engineers, 345 East 47th Street, New York, NY 10017.

[5] CAN/CSA Z234.1-89, *Canadian Metric Practice Guide*, Canadian Standards Association, 178 Rexdale Blvd., Etobicoke, Ontario, Canada M9W 1R3.

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TABLE 1-6. SI DERIVED UNITS' SPECIAL NAMES AND SYMBOLS.

Derived quantity	Special name	Special symbol	Expression in terms of other SI units	Expresson in terms of SI base units
force	newton	N		$m \cdot kg/s^2$
pressure, stress, energy, work	pascal	Pa	N/m^2	$kg/m \cdot s^2$
quantity of heat	joule	J	$N \cdot m$	$kg \cdot m^2/s^2$
power, radiant flux	watt	W	J/s	$kg \cdot m^2/s^3$

TABLE 1-7. DECIMAL MULTIPLES AND SUBMULTIPLES OF SI UNITS: SI PREFIXES

Factor	Prefix	Symbol	Factor	Prefix	Symbol
$10^{24} = (10^3)^8$	yotta	Y	10^{-1}	deci	d
$10^{21} = (10^3)^7$	zetta	Z	10^{-2}	centi	c
$10^{18} = (10^3)^6$	exa	E	$10^{-3} = (10^3)^{-1}$	milli	m
$10^{15} = (10^3)^5$	peta	P	$10^{-6} = (10^3)^{-2}$	micro	μ
$10^{12} = (10^3)^4$	tera	T	$10^{-9} = (10^3)^{-3}$	nano	n
$10^9 = (10^3)^3$	giga	G	$10^{-12} = (10^3)^{-4}$	pico	p
$10^6 = (10^3)^2$	mega	M	$10^{-15} = (10^3)^{-5}$	femto	f
$10^3 = (10^3)^1$	kilo	k	$10^{-18} = (10^3)^{-6}$	atto	a
10^2	hecto	h	$10^{-21} = (10^3)^{-7}$	zepto	z
10^1	deka	da	$10^{-24} = (10^3)^{-8}$	yocto	y

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CHAPTER 2

Safety Considerations for Compressed Gases and Cryogenic Liquids

INTRODUCTION

The very properties that make compressed gases and cryogenic liquids useful in almost every area of modern life can also cause hazardous conditions if mishandled. These hazards may vary with the characteristics of the product and how it is stored. Storing gases under high pressure or at cold (cryogenic) temperatures may create a hazard. Gases may be flammable, corrosive, toxic, self-reactive, or cause an explosion. They also may be oxidizing, pyrophoric, or cause asphyxiation.

Personnel potentially exposed to the hazards while producing, using, handling or transporting these products must be well trained and knowledgeable. They must know how to respond if a potentially harmful incident occurs.

There is a great deal of information available on the physical and chemical properties of compressed gases and cryogenic liquids and the precautions to follow for their safe storage, transport, handling, and use. Years of experience with these products have resulted in numerous safety regulations, standards, guidelines, product and equipment specifications, and recommended practices and procedures.

This chapter describes many of the potential hazards associated with compressed gases and cryogenic liquids, and presents some of the requirements and guidelines for their safe handling, use, and transportation. However, the information is not complete with respect to all types of gases or containers, and some applications require additional safety precautions. More detailed information may be found in other sections of this handbook, references cited in Appendix 6, and at the end of this chapter.

CONTENT IDENTIFICATION/ PRODUCT LABELING AND INFORMATION

Good safety begins with proper identification of the container contents. Containers must have a legibly printed label identifying the contents and giving precautionary warning to the user who is responsible for the handling of the container and connecting it for use. Containers offered for shipment must have their contents identified in accordance with U.S. Department of Transportation (DOT) and the Occupational Safety and Health Administration (OSHA) Hazard Communication Standards (29 CFR 1910.1200) [1]. In Canada, identification shall be in compliance with the *Transportation of Dangerous Goods* (TDG) *Regulations* [2], *Hazardous Products Act*, *Controlled Products Regulations* and the *Provincial Workplace Hazardous Materials Information System* (WHMIS) *Regulations.* Appendix A of CGA C-7, *Guide to the Preparation of Precautionary Labeling and Marking of Compressed Gas Containers*, also provides guidance on product identification [3].

Color alone must not be used to identify container content. The primary identifier is the

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container label and DOT/TC product markings. See CGA PS–2, *CGA Position Statement Establishing an Industry Standard Color Code for Compressed Gas Cylinders* [4]. Even though the medical gas industry adopted a color code to aid in the identification of medical gas cylinders, the user must not rely solely on color coding to identify cylinder contents. See CGA C-9, *Standard Color Marking of Compressed Gas Containers Intended for Medical Use*, and Canadian General Standards Board 24.2-M86, *Standard for Identification of Medical Gas Containers, Pipelines and Valves* [5, 6].

Containers not bearing a legibly written, stamped, or stenciled identification of contents must not be transported, handled, or used. They should be segregated for return to the gas supplier or distributor. Labels identifying the product content should be applied before removal of the container from the filling manifold or when mixtures are analyzed.

Requirements for marking, labeling, inspection, testing, filling, and disposition of cylinders are covered in Chapter 9. For further details, refer to CGA C-7, CGA P-1, *Safe Handling of Compressed Gases in Containers*, CGA P-15, *Filling of Industrial and Medical Nonflammable Compressed Gas Cylinders*, and CGA P-22, *The Responsible Management & Disposition of Compressed Gases & Their Containers* [3, 7, 8, 9].

Detailed information regarding the physical and chemical properties, specific handling, safety precautions, physiological effects on humans, and emergency procedures (including special fire fighting considerations) are covered in the individual gas monographs in Part II and Material Safety Data Sheets (MSDSs) developed by the manufacturer for each product and available through the supplier.

SAFE HANDLING, USE AND STORAGE

Because of the tremendous variety of compressed gas products, containers, and related equipment, it is important that they be stored, handled, and used only in accordance with applicable regulatory requirements, manufacturer recommendations, CGA standards, and associated guidelines for the specific product and containers involved.

Handling and use

Practices and precautions that must be followed when handling and using compressed gas containers include:

- Containers should be moved by means of a hand truck, forklift truck, cylinder pallet system, or other device designed to minimize the risk of containers dropping or violently striking against each other or other objects. Filled containers or those having residual product must not be moved by rolling or dragging in a horizontal position, or moved or lifted by the valve or valve protection cap. Magnets should never be used as lifting devices.
- Ropes, chains or slings must not be used to lift or suspend containers unless, at the time of manufacture, provisions were made to include appropriate lifting attachments such as lugs. In the absence of such manufactured lifting attachments, suitable cradles or platforms must be used for lifting.
- Containers must not be dropped or slid in a way that damages the cylinder walls or allows sharp objects to damage the cylinder walls. Leaking, damaged or defective containers should not be shipped without authorization from the gas supplier.
- Container maintenance and repair including painting; removal or defacing of product markings or labels; and removal, modification, alteration, blockage or replacement of valves or pressure relief devices must be performed only by trained personnel under the direction and consent of the container owner or an authorized representative.
- Care must be taken to prevent the container from being damaged by an electric arc. This requires that containers not be placed or used in a manner where they can

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become part of an electrical circuit. When used in proximity to electric welding, they must not be grounded or used for grounding.

- Compressed gas containers must not be exposed to direct heat, flame, or temperature extremes. Temperatures above 125°F (51.7°C) may result in excessive cylinder pressure and damage the container's physical integrity. If ice or snow accumulates on a container, thaw at room temperature. If containers are exposed to fire or struck by an electric arc, notify the gas supplier and obtain authorization from the supplier to ship such containers.
- Containers exposed to artificially created low temperatures (for example, refrigeration units) may undergo significantly decreased impact resistance and ductility. Get approval from the supplier before subjecting the container to such extremes.
- Where containers are designed to accept a valve protection cap, the cap must be maintained in a secured position on the container except when the container is secured and connected for use.
- Where provided, valve outlet caps or plugs should be securely affixed to the valve outlet prior to transportation. For certain materials (for example, Division 2.3), gastight caps or plugs must be used since they provide a secondary seal for the valve. It is required that these plugs be checked and tightened securely prior to returning to the gas supplier.

Storage

Safe storage of compressed gases begins with posting signs identifying storage locations for gases or cryogenic liquids. Identification can be by name, by hazard class, or both, or by some other comparable identification method where mandated by federal, state, provincial or local ordinance. In addition, warnings such as "NO SMOKING" should be conspicuously posted where appropriate. Other safe storage considerations include:

- Storage areas must be well drained and well ventilated, and preferably of fire-resistive construction. Storage area temperatures must not allow cylinder temperatures to exceed 125°F (51.7°C).
- Adequate spacing or segregation by partitioning should be provided allowing containers to be grouped together by the hazard class of the gas. Additional consideration should be given to separate storage, or segregation of full and empty containers.
- Storage in subsurface locations or enclosed spaces such as basements should be avoided. Users of compressed gas products must ensure there is adequate separation from combustibles as specified by federal, state, provincial, and local regulations. Containers should not be stored near flammable substances such as gasoline.
- Containers should not be exposed to corrosive chemicals or fumes. Corrosion may damage the containers and may make the container valve protection caps difficult to remove.
- Containers must not be stored where moving objects may strike or fall on them, and they must be secured.
- Containers stored or used in public areas must be protected against tampering and unauthorized access..
- Medical gases should not be stored in an operating room.
- Containers may be stored outdoors, but prolonged exposure to a damp environment should be avoided. Containers should not be exposed to salt, or corrosive chemicals and fumes.
- It is preferable to store containers on paved surfaces such as concrete, that has been graded to prevent the accumulation of water. However, asphalt or hydrocarbon-based paving materials should be avoided in storage areas for liquid oxygen containers to avoid violent reaction in the event of a leak.
- Compressed gas cylinders in service or storage at user locations must be secured

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to prevent falling. At gas supplier and distributor facilities, the nesting of cylinders is considered an equivalent safe manner of storage. See CGA P-1 [7]. However, nesting of cylinders may not be adequate in seismically active areas, and additional measures may be required to prevent cylinders from falling.

See the section in this chapter on Hazards for additional information on recommended safety practices for each hazard class.

CONNECTING CONTAINERS FOR FILLING, TRANSFERRING OR WITHDRAWING CONTENTS

Before using, making a connection to fill, transferring, or withdrawing product from a compressed gas or cryogenic liquid container, always first identify the container content by checking for any markings and a legibly written label. Never connect, fill, withdraw, or use a product when the container content is unknown. Any such containers should be identified, segregated, and the gas supplier notified.

Container filling

In the United States, containers filled for the transportation of compressed gases must comply with DOT regulations. In Canada, the filling requirements of containers are governed by Transport Canada's (TC) TDG Regulations. DOT regulations published in Title 49 of the U.S. *Code of Federal Regulations* (49 CFR) and similar regulations published by TC in the TDG Regulations require that compressed gas containers must not be transported or filled without the owner's consent, that such cylinders must be periodically inspected and tested to ensure they are in safe condition for filling, and that filling shall be undertaken only by properly qualified personnel [10, 2]. Each cylinder must bear the proper DOT or TC labels and markings to identify the product contained.

The transfer of compressed gases from one container to another should only be performed by the gas supplier or personnel who are trained and qualified with both the proper transfill equipment and written operating procedures. They should be familiar with the necessary precautions to avoid the hazards of the product and with the procedures necessary to comply with government standards and regulations.

Detailed written operating instructions, including equipment inspection and maintenance procedures, should be provided by the supplier of the transfill equipment and scrupulously followed. Transfilling of gaseous and liquid oxygen for respiration is allowed when permitted by the container owner and when carried out in accordance with CGA P-2.5, *Transfilling of High Pressure Gaseous Oxygen to be Used for Respiration*, and P-2.6, *Transfilling of Liquid Oxygen to be Used for Respiration* [11, 12].

At gas manufacturing facilities a checklist or operating procedures should be posted or available to guide those who fill containers. Procedures will vary depending on the type of cylinder and product (for example, high pressure compressed gas cylinders versus liquefied compressed gases). The checklist questions to answer should include:

- proper markings, labels?
- potentially unsafe cylinder conditions (cracks, burns, corrosion, gouges)?
- oil or grease contamination?
- valve outlet connections for cleanliness or damage?
- damaged or plugged pressure relief device?
- impurities or contaminants in the cylinder?
- venting cylinder contents through devices meeting environmental requirements?
- evacuation of cylinders to remove contaminants?
- internal corrosion?
- proper filling quantity?
- leaks?
- correct content label?
- outlet cap or gas-tight plugs or caps?

In accordance with CGA C-10, *Recommended Procedures for Changes of Gas Service for Compressed Gas Cylinders,* only a gas supplier can change gas service for a cylinder [13]. Nonrefillable cylinders (DOT 39, DOT 2P and

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DOT 2Q) must not be refilled with any material. After using, such cylinders must be disposed of in accordance with the cylinder manufacturer's recommendations [9].

Connecting container(s) and withdrawing contents

In the United States and several other countries, the industry has developed standardized cylinder valve outlet and inlet connections, transfer connections, and regulator connections for specific types and groups of compressed gases to prevent the misapplication of these potentially hazardous materials.

Container valve connections that do not fit must not be forced. Threads on regulator connections or other auxiliary requirements must match those on the container valve outlet. The valve outlet connection should conform to recognized standards such as ANSI/CGA V-1, *American National, Compressed Gas Association Standard for Compressed Gas Cylinder Valve Outlet and Inlet Connections* [14]. However, it must be acknowledged that connections other than those found in ANSI/CGA V-1 may exist. If a user chooses such a connection, extreme care must be taken to ensure that such connections do not cross-connect with existing connections in ANSI/CGA V-1, and that they have been properly engineered for the intended gas service and pressure. The threads on a cylinder valve outlet, as well as on regulators and other ancillary equipment, should be examined at frequent intervals to ensure they are clean and undamaged.

Container valves must be kept closed at all times whether the cylinder is full or empty except when the container is in use. When the valve is opened, it must be opened slowly. The valve outlet must be pointed away from all personnel during opening since a compressed gas stream directed toward someone may cause injury to their eyes or body.

Some container valves do not have handwheels. Special wrenches provided or recommended by the gas supplier must be used. These wrenches must remain on the valve while the container is in use. Other wrenches, hammers, or tools (except torque wrenches designed for this use) must not be used to open or close valves on containers. Contact the gas supplier if a valve is difficult to operate.

Medical gas cylinders may be equipped with either handwheel-operated valves or post-type valves. Make sure that the threads on regulator-to-cylinder valve connections or the pin-indexing devices on yoke-to-cylinder valve connections are properly mated. Never force connections. The cylinders on which the post valves are mounted may not be equipped with any valve protection cap or valve guard. Since these cylinders are generally small enough to be carried with one hand, they are very vulnerable to being dropped. Dropping such cylinders on a hard surface in an inverted or near inverted position can result in serious damage to the valve operating parts possibly resulting in the expulsion of the valve stem, which can cause severe injuries. Valves damaged by dropping should cause the cylinder to be removed from service, properly vented, and the valve repaired or replaced. For further details concerning safe handling of medical gases, refer to CGA P-2, *Characteristics and Safe Handling of Medical Gases*, and the audiovisual training program CGA AV-4 of the same title [15].

Unless provided with a back-flow prevention system, compressed gas containers must not be connected to process piping where the container may be contaminated by the backflow of other process materials. Certain noncryogenic liquefied gases may be especially susceptible to this type of contamination due to their relatively low vapor pressures at ambient temperatures. In cases where such a possibility may exist, design consideration must include the use of check valves or traps, or both for this purpose.

The release of high-pressure gas from cylinders can be hazardous unless adequate means are provided for reducing the gas pressure to usable levels and for controlling the gas flow. Accordingly, pressure-reducing regulators should always be used when withdrawing the contents of a cylinder because such devices deliver a constant safe working pressure.

A suitable pressure-regulating device and pressure relief device must be used where gas is admitted to a container or system of lower pressure rating than the supply pressure, and where, due to the gas capacity and pressure of the supply source, the operating or working

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system pressure rating may be exceeded. This is a requirement regardless of the presence of a pressure relief device protecting the lower pressure system.

Likewise, a suitable pressure relief device must be used to protect a container or system using a compressed gas where the system has a pressure rating lower than the compressed gas supply source, and where, due to the gas capacity of the supply source, the system pressure rating may be exceeded.

When using a compressed gas (except acetylene) from a container, the regulator pressure setting should not be set below the operating pressure of the system or not less than 20 psig (138 kPa) to prevent backflow of atmospheric air or other contaminants into the container. Acetylene must never be used in its free state at pressures in excess of 15 psig (103 kPa). The container valve must be closed hand-tight to retain this residual pressure.

Where compressed gas containers are connected to a manifold, the manifold and its related equipment such as regulators and safety devices must be of the proper design for the product(s) they are to contain at the appropriate temperatures, pressures, and flows.

Piping, regulators and other apparatus must be kept gas-tight to prevent leakage. This can be confirmed by the use of a compatible leak-test solution, or an appropriate leak-detection instrument.

Caution: The system should be depressurized before tightening connections, repairing leaking fittings, or attempting other repairs.

Caution: Before removing a regulator from a container, the container valve must be closed and the regulator relieved of gas pressure.

Regulators, gauges, hoses and other apparatus provided for use with a particular gas or group of gases must not be used on containers of gases having different chemical properties or service pressure ratings unless information from the gas supplier indicates this may be done safely. As an example, only pressure regulating devices approved for use with oxygen can be used in oxygen service.

Before returning an empty container to a supplier, the cylinder valve must be closed and the pressure regulator and piping disconnected. If provided, the gas-tight plug or cap must be replaced.

Pressure-regulating devices, pressure relief devices, valves, cylinder connections, and hose lines should be inspected at frequent intervals to ensure they are undamaged and in safe working condition. Compressed gas containers with devices and appurtenances that appear to be damaged in any way should not be used, and the supplier should be contacted for instructions on the disposition of the container.

Detailed information regarding compressed gas containers, pressure regulators, pressure relief devices, and valve outlet connections is contained in Chapters 5 through 9. Additional safe handling procedures for compressed gases can be found in CGA P-1 [7], and in CGA AV-1, an audiovisual safety training program of the same title.

HAZARDS

Gases are classified based upon their health and physical hazards. Personnel using gases must have a thorough knowledge of their properties to maintain a safe operation.

Gases may present a potential hazard because they are:

- Under high pressure
- Extremely cold (cryogenic liquids)
- Flammable
- Asphyxiants (inert)
- Oxidizers
- Toxic
- Corrosive
- Pyrophoric

Some gases may combine several of the above hazards. For example, a cylinder of hydrogen gas combines high pressure with the flammable hazard. Liquid oxygen combines the oxidizer with the low-temperature hazard.

A brief description of the main classifications follows. More information on specific gases found in each class can be found in the gas monographs in Part II of this handbook, or by consulting the MSDS developed by the manufacturer for each product and available through the supplier.

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Under high pressure

Depending on the pressure rating of the container and system components, compressed gases may be pressurized in excess of 6000 psig (41 380 kPa). Containers or piping that are pressurized beyond their marked service pressure or allowable working pressure are subject to catastrophic failure. It is important to always use the appropriate pressure-regulating and pressure relief devices to prevent overpressurization.

Gas venting from the cylinder valve outlet or other points of leakage is a hazard to personnel using the cylinder. A high-pressure gas stream can penetrate the skin causing serious injury; the eyes and face are extremely vulnerable. Valve outlets should be directed away from the body when being opened. The use of goggles or a face shield is also recommended.

Extremely cold (cryogenic liquids)

Cryogenic liquids are gases that have been transformed by refrigeration into extremely cold liquids, which are stored at temperatures below –130°F (–90°C). They are stored at low pressures in specially constructed, multiwalled, vacuum-insulated containers.

Examples of gases commonly handled as cryogenic liquids include oxygen, nitrogen, argon, neon, hydrogen, and helium. Liquefied natural gas (LNG), liquid methane, and liquid carbon monoxide are also handled as cryogenic liquids. The consequences from extreme cold and other potential hazards that accompany these products are:

- extreme cold that can freeze human tissue on contact, and can also cause embrittlement of carbon steel, plastics, and rubber;
- container or piping failure resulting from overpressure;
- asphyxiation due to displacement of oxygen by escaping liquid and the resultant rapidly expanding gas (in the case of inert gases);
- fire or explosion caused by escaping flammable gases such as hydrogen, carbon monoxide, or methane; and
- fire or explosion from escaping liquid oxygen, which, while not itself a flammable gas, can combine with organic materials with explosive violence.

To handle cryogenic liquids safely, it is important to know the physical and chemical properties of these products. Table 2-1 is a useful guide to the physical properties of commonly used cryogenic liquids. Table 2-2 shows the basic fire extinguishing agents used on cryogenic liquids. Table 2-3 is a guide to the flammable and fire hazards of common cryogenic liquids. For more detailed information, refer to the individual gas monographs in Part II for the particular cryogenic liquid in question.

Because of the potential hazards resulting from the extremely low temperatures of cryogenic liquids, all personnel using them must be properly trained in the use of specialized equipment designed for the safe storage, transfer, and handling of these products.

Heavy leather protective gloves, safety shoes, aprons, and eye protection must be worn to prevent possible contact with the extremely cold gas or surfaces of uninsulated piping, transfer connections, valves, and other equipment, or from the cold liquid or boil-off vapors that may result from spilled or splashed liquid.

Any transfer operations involving open containers such as dewars must be conducted slowly to minimize boiling and splashing of the cryogenic liquid. Such operations must be carried out only in well-ventilated areas to prevent the possible accumulation of inert gas, which can displace the oxygen in the atmosphere and cause asphyxiation.

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Cryogenic liquids must be handled and stored only in containers and systems specifically designed for these products and in accordance with safe practices as described in CGA P-12, *Safe Handling of Cryogenic Liquids* [16]. Cryogenic liquid containers are described in Chapter 5.

Equipment and systems designed for the storage, transfer, and dispensing of cryogenic liquids must be constructed of materials compatible with the products handled and the temperatures encountered. All such systems must be equipped with pressure relief devices to prevent excessive pressure buildup due to the vaporization of the cryogenic liquid as heat leaks into the system. Piping must be equipped with pressure relief devices that prevent the potential buildup of excessive pressure due to vaporiza-

TABLE 2-1. PHYSICAL PROPERTIES OF CRYOGENIC LIQUIDS

Gas Chemical Symbol	Ethylene C_2H_4	Xenon Xe	Krypton Kr	Methane CH_4	Oxygen O_2	Argon Ar	Carbon Monoxide CO	Nitrogen N_2	Neon Ne	Hydrogen H_2	Helium He
Boiling Point, 1 atm (101.325 kPa, abs)											
°F	−154.8	−163	−244	−259	−297	−303	−313	−320	−411	−423	−452
°C	−103.8	−108	−153	−161	−183	−186	−192	−196	−246	−253	−268
Melting Point, 1 atm (101.325 kPa, abs)											
°F	−268	−169	−251	−296	−362	−309	−341	−346	−416	−435	(1)
°C	−167	−112	−157	−182	−219	−189	−207	−210	−249	−259	
Density at boiling point and 1 atm (101.325 kPa, abs)											
lb/cu ft	35.42	191	151	26	71	87	49	50	75	4.4	7.8
(kg/m^3)	(567.47)	(3059.5)	(2418.8)	(416.5)	(1137.3)	(1393.6)	(784.9)	(800.9)	(1201.4)	(70.48)	(124.94)
Heat of vaporization at boiling point											
Btu/lb	208	41.4	46.2	219.2	91.7	69.8	92.8	85.6	37.1	191.7	8.72
(kJ/kg)	(484)	(96.3)	(107.5)	(509.91)	(213)	(162.3)	(215.8)	(199.1)	(86.3)	(446)	(20.28)
Volume expansion Ratio, liquid at 1 atm (101.325 kPa, abs) and boiling point to gas at 70 °F (21.1 °C) and 1 atm (101.325 kPa, abs)	450	559	693	625	860	842	680	696	1445	850	745
Flammable	Yes	No	No	Yes	No (2)	No	Yes	No	No	Yes	No

Notes:

(1) Helium does not solidify at 1 atm pressure.

(2) Oxygen does not burn, but supports and accelerates combustion. However, high concentration oxygen atmospheres substantially increase combustion rates of other materials, and may form flammable mixtures with other combustibles. Flame temperatures in oxygen are higher than those in air.

TABLE 2-2. FIRE EXTINGUISHING AGENTS FOR CRYOGENIC LIQUID IN FIRE.

Extinguishing Agent	Cryogenic Liquids	
	Oxygen	Hydrogen, Methane, Carbon Monoxide, Ethylene
Water	Preferred	Used to protect adjacent equipment or property and to spray personnel. Not to be applied directly onto burning vapor or cryogenic liquid, since the water will evaporate additional flammable material.
Soda Acid	Unacceptable	Unacceptable.
CO_2	Unacceptable	Fair. Apply at base of flame.
Dry Powder	Unacceptable	Good. Apply at base of flame.
Methyl Bromide	Unacceptable	Not normally used unless authorized and supplied for individual premises or equipment.

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TABLE 2-3. FLAMMABLE AND FIRE HAZARDS OF COMMON CRYOGENIC LIQUIDS

	Oxygen	Nitrogen	Argon	Helium	Krypton	Xenon	Neon	Methane	Hydrogen	Carbon Monoxide	Ethylene
Flammable hazard with combustible materials	Yes	No	No	No	No	No	No	Yes	Yes	Yes	Yes
Explosive hazard with oxygen or air	—	No	No	No	No	No	No	Yes	Yes	Yes	Yes
Pressure rupture if liquid or cold vapor is trapped	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	(within flammable limits) Yes	Yes	Yes
Fire Hazard type											
Combustible	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Yes	Yes	Yes	Yes
Promotes ignition	Yes	No	No	No	No	No	No	Yes	Yes	Yes	Yes
Condenses air and expands flammable range	No	Yes	No	Yes	No	No	Yes	No	Yes	No	No
Flammable limits in air, Percent by volume	—	—	—	—	—	—	—	5-15	4-75	13-74	2.7-36
Spontaneous ignition temperature in air at 1 atm (101.325 kPa, abs)											
°F	—	—	—	—	—	—	—	1000	1085	1204	914
°C	—	—	—	—	—	—	—	538	585	651	490
Minimum ignition energy, mJ	—	—	—	—	—	—	—	0.30 0.45	0.02		0.08
Flame temperature in air	—	—	—	—	—	—	—				
°F	—	—	—	—	—	—	—	3407	3722	3812 (1)	3781
°C								1875	2050	2100	2088
Flame velocity in air											
ft/sec	—	—	—	—	—	—	—	1.28	8.9	1.08	2.07
cm/sec	—	—	—	—	—	—	—	39	271	33	63
Limiting oxygen index volume, (2)											
Percent	—	—	—	—	—	—	—	12	5	5.7	10

Notes:

(1) The maximum flame temperature for carbon monoxide occurs at about the stoichiometric mixture (66.6% carbon monoxide, 33.33% oxygen). The range of flame temperatures is 1560 °C to 2100 °C.

(2) Minimum oxygen concentration to support flame propagation when stoichiometric fuel-air mixture is diluted with nitrogen.

tion of liquid when trapped between valves in piping. Only materials designed for cryogenic service should be used.

Caution: Do not smoke or permit smoking or open flames in any area where cryogenic, flammable, or oxidizing liquids or gases are stored, handled, or used, or where they are loaded or unloaded.

Special precautions for liquid oxygen

Liquid oxygen containers, piping, and equipment must be properly cleaned for oxygen service and must be kept clean and free of grease, oil, or other hydrocarbon materials, which can combine with oxygen with explosive violence. Detailed information on methods of

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cleaning is provided in CGA G-4.1, *Cleaning Equipment for Oxygen Service* [17], and in Chapter 11 of this handbook. Liquid oxygen systems at consumer sites must comply with NFPA 50, *Standard for Bulk Oxygen Systems at Consumer Sites* [18]. (See Fig. 2-1.)

Caution: Keep all combustible materials, especially oil and grease, away from oxygen.

While oxygen is nonflammable, it vigorously accelerates and supports combustion. Do not permit liquid oxygen or oxygen-rich air atmospheres to come in contact with organic materials or flammable substances of any kind.

Among the organic materials that can react violently with oxygen or oxygen-rich atmospheres when ignited are oil, grease, asphalt, kerosene, cloth, tar, and dirt that may contain oil or grease. A single hot spark can be sufficient to trigger ignition of these materials when in contact with an oxygen-rich atmosphere. If liquid oxygen spills on asphalt or other combustible substances (for example, oil-soaked concrete or gravel), do not walk on or roll equipment over the area of the spill because the impact or pressure may cause ignition. Keep all sources of ignition away for at least 30 minutes after all frost or fog has disappeared.

Note: Neither liquid nor gaseous oxygen can be effectively blanketed by such fire extinguishing agents as carbon dioxide, dry chemical, or foam. If a fire should occur where liquid or gaseous oxygen is present, it is necessary to cool combustible materials below their ignition temperatures to stop the fire. One method of doing this is to use large quantities of water in spray form.

Caution: Liquid oxygen, if spilled on clothing or another combustible substance, can pose a serious hazard of fire or explosion due to the rapid chemical reaction between the two substances.

If liquid oxygen is spilled on clothing, the clothing must be removed at once and aired before reuse. Areas where liquid oxygen may be spilled during transfer operations must be free of hydrocarbons or other combustible materials.

For additional information on the handling of oxygen, refer to the section entitled Oxygen and Oxidizing Gases later in this chapter, and to the monograph on oxygen in Part II.

Special precautions for Liquefied Natural Gas (LNG)

Any area where LNG is stored must be posted NO SMOKING—FLAMMABLE GAS. Open flames and general-purpose electrical equipment must be prohibited. Storage and transfer must be under positive pressure to prevent infiltration of air and other gases. LNG systems at utility plants and consumer sites must comply with NFPA 59A, *Standard for the Production, Storage and Handling of Liquefied Natural Gas (LNG)* [19]. For additional information on safe handling of LNG, refer to the monograph on methane in Part II.

Special precautions for liquid hydrogen

Liquid hydrogen is highly flammable and should be stored, transferred, and handled out-of-doors unless a specific review for safe handling indoors has been made. Where liquid hydrogen is stored or handled, smoking, open flames, and unclassified electrical equipment must be prohibited, and the area must be marked NO SMOKING–FLAMMABLE GAS. Liquid hydrogen must be stored and transferred only in equipment specially designed for hydrogen service and under positive pressure to prevent the infiltration of water vapor or air and subsequent solidification. Liquid hydrogen systems at consumer sites must comply with NFPA 50B, *Standard for Liquefied Hydrogen Systems at Consumer Sites* [20]. For additional information on safe handling of liquid hydrogen, refer to the monograph on hydrogen in Part II.

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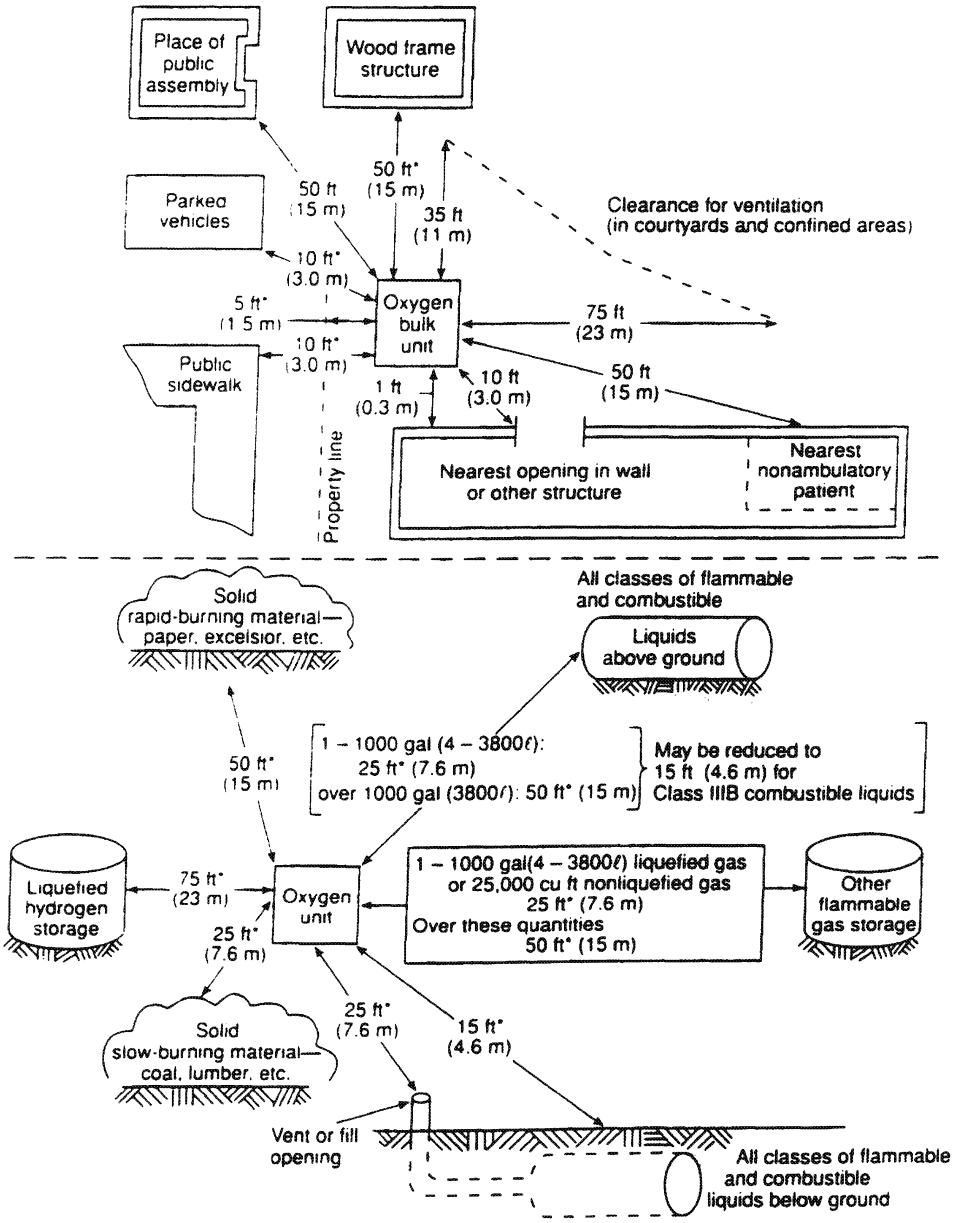

*NOTE. These distances do not apply where protective structures having a minimum fire resistance rating of two hours interrupt the line-of-sight between uninsulated portions of the bulk oxygen storage installation and the exposure. The protective structures protect uninsulated oxygen storage containers or supports, control equipment, and system piping (or parts thereof) from external fire exposure. Liquid oxygen storage containers are insulated. Such containers may provide line-of-sight protection for uninsulated system components. Interruption of the line-of-sight means that an "eye" on any part of the uninsulated portion of the bulk oxygen storage installation cannot "see" any part of the exposure.

Fig. 2-1. Distances between bulk oxygen systems and exposures. (Reprinted with permission from NFPA 50, *Standard for Bulk Oxygen Systems at Consumer Sites*, Copyright © 1996, National Fire Protection Association, Quincy, MA 02269. This reprinted material is not the complete and official position of the NFPA on the referenced subject, which is represented only by the standard in its entirety.

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Special precautions for liquid helium

Liquid helium must be stored and transferred only under positive pressure to prevent the infiltration of air and solidification of water vapor or air. Otherwise, the backflow of air into liquid helium vessels and equipment can create blockage of openings that may lead to rupturing of the container. Transfer piping for liquid helium must either be insulated or must be provided with a noncombustible tray to prevent liquid air condensed on the piping from contacting asphalt or other hydrocarbon materials. For additional information on liquid helium and other inert cryogenic liquids refer to the individual gas monographs in Part II. Detailed information concerning the safe handling of the various inert, oxidizing, and flammable cryogenic liquids can be found in CGA P-12 [16].

Flammable gases

Flammable gases are defined by DOT and TC as those gases that when mixed with air in concentration of 13 percent or less (by volume) form a flammable mixture, or the flammable range with air is wider than 12 percent regardless of the lower limit. To ignite a flammable gas, the three basic conditions simultaneously needed are concentrations of the gas (fuel) within the flammable limits, air/oxidizer, and source of ignition. Examples of flammable gases include acetylene, 1,3-butadiene, carbon monoxide, ethane, ethylene, hydrogen, hydrogen sulfide (toxic and flammable), liquefied petroleum gases (butane, isobutane, propane and propylene), methane, methylacetylene propadiene (MAPP liquid), methlychloride, silane, and vinyl chloride. The amount of flammable material is respectively much greater per unit volume when a flammable gas is stored in liquefied form under its own vapor pressure.

Storage facilities

Facilities containing flammable gases shall be protected from hazardous exposures such as adjoining buildings, equipment, property, incompatible materials, and concentrations of people in accordance with the building code and fire code. Storage and use areas should be adequately ventilated in accordance with the fire code and mechanical code. Electrical equipment shall be provided in accordance with the electrical code. Ignition sources and clearance from combustible materials shall be controlled in accordance with the fire code. Specified exposures, such as incompatible materials can be separated using a 1-hour fire resistive noncombustible partition.

The construction of walls, partitions, ceilings, openings, and rooms with other building occupancy shall be in accordance with the building code. In Canada, national, provincial, and local codes shall apply.

Liquefied flammable compressed gases shall be stored and used with the pressure relief device in direct contact with the vapor phase. Some cylinders are designed for such storage and use in the horizontal position such as those designed for forklifts and tow motors.

Special precautions for acetylene

Acetylene is a highly reactive flammable gas and can be stored safely only in cylinders specially designed for acetylene service. Acetylene containers should be stored valve end up. Gas suppliers and distributors may store properly secured containers in a horizontal position. For details on the chemical and physical properties of acetylene, the special design of acetylene cylinders, and safe handling and emergency procedures to be followed, refer to the monograph on acetylene in Part II.

Portable fire extinguishers (carbon dioxide or chemical types), or other fire protection or suppression systems or devices must be available for fire emergencies at storage installations. Only trained personnel should be allowed to operate fire extinguishers. A flame-producing device must never be used for detection of flammable gas leaks. Either a flammable gas detector or compatible leak detection solution should be used.

Emergency plan

In the event of an emergency situation involving a flammable gas (whether a gas leak, fire, or explosion), personnel should immediately evacuate the area. If the facility is equipped with a sprinkler system, activate the

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system as the evacuation is underway. Do not attempt to extinguish burning gas if the flow of product cannot be shut off immediately and without risk. Contact the fire department and other appropriate emergency response agencies immediately. Rescue or other emergency response activities should only be attempted by trained and qualified personnel.

Any facility where flammable gases are stored or handled should have a thorough training program for all employees on what to do in a fire emergency. Such a program should include frequent fire drills, proper location and upkeep of fire emergency equipment, and liaison between the facility's emergency response personnel and local fire department personnel.

An emergency plan should be developed with sketch maps and diagrams showing the locations of stored flammable materials, fire alarms, personnel gathering points, emergency exits, escape routes, rescue and safety equipment, hydrants, fire equipment, and plant controls to be activated in the event of a fire emergency. All personnel should be aware of special or unusual risks associated with stored flammable materials.

While it is not possible to outline specific fire emergency techniques that will cover all types of fires involving flammable gases or cryogenic liquids, some general rules should be observed.

- Everyone not actively engaged in responding to the fire emergency should be evacuated from the area.
- If a flammable cryogenic liquid is spilled, the flammable mixture zone may extend beyond the normal fog cloud produced by condensing water vapor in the air. Personnel should be evacuated well outside the fog area to an upwind location.
- The single best fire fighting technique is to shut off the flow of flammable liquid or gas.
- If electrical equipment is involved, be sure that the power supply is disconnected before using water to fight the fire, or use carbon dioxide or dry chemical extinguishers to fight the fire. *Note:* Fires involving fuel supported by liquid or gaseous oxygen cannot be effectively blanketed by such agents as carbon dioxide, dry chemical, or foam. It is necessary to cool combustible materials below their ignition temperatures to stop the fire. In such cases, use large quantities of water in spray form.
- Use the water spray to cool any combustible material below its ignition temperature. If possible do not spray cold areas of equipment or direct water into a cryogenic fluid. Fire hoses with stream-to-spray nozzles should be available where large quantities of flammable liquefied gases or cryogenic liquids are handled. With hydrogen, do not spray water into or onto the vent stack or relief valve of liquid hydrogen tanks.
- It is usually not advisable to extinguish a flammable cryogen in a confined area. If the flammable gas supply cannot be shut off, the continued escape of unignited gas can create an explosive mixture. Other burning material or hot surfaces may reignite this mixture. In such cases, it is usually better to allow the gas to burn itself out in a confined area and keep adjacent objects cool with water, rather than risk exposing personnel at the site to a potential explosion.
- If an inert cryogenic liquid is leaking or venting, the decision to try shutting off the gas flow by the associated valving should take into account the amount of risk of asphyxiating fire fighters in the process. ***Caution:*** Pressure relief devices should not be blocked or prevented from operating.

Flammable compressed gas systems (piping, tubing, fittings, gaskets, and thread sealants) must be suitable for the applicable flammable compressed gas service and for the pressures and temperatures involved. Material specifications and thickness requirements for piping and tubing must conform to the American Society of Mechanical Engineers Code ANSI/ASME B31.3, *Chemical Plant and Petroleum Refinery Piping* [22]. All piping and equipment associated with flammable gas systems must be grounded and bonded. Nonsparking tools must be used when working with or on flammable compressed gas cylinders/systems.

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Further specific information for handling flammable gases can be found in the individual gas monographs provided in Part II.

Asphyxiant gases (including inerts)

Asphyxiant gases, which include inert gases, such as argon, carbon dioxide, helium, krypton, neon, nitrogen and xenon can displace oxygen in air and can cause rapid suffocation due to oxygen deficiency. Depletion of the normal oxygen content in air (approximately 21 percent) either by combustion or displacement with inert gas, is a serious potential hazard to personnel. When the oxygen content of air is reduced to 15 percent or below, an individual breathing the air may be mentally incapable of diagnosing the situation because sleepiness, fatigue, lassitude, loss of coordination, errors in judgment, and confusion masked by a state of euphoria will give the victim a false sense of security and well-being.

Caution: Human exposure to atmospheres containing 12 percent or less oxygen will bring about unconsciousness without warning so quickly that the individual cannot react to evacuate or use an air-line respirator or SCBA. This is true whether the oxygen-deficient condition is reached by an immediate change of environment or by gradual depletion of oxygen in the atmosphere.

Inert gases handled as cryogenic liquids can, if released, generate extremely large volumes of inert gas, which can rapidly displace the oxygen in the atmosphere. For example, one volume of liquid nitrogen at its boiling temperature at 1 atm, vaporizes to 696.5 volumes of nitrogen gas when warmed to room temperature (70° F or 21.1° C at 1 atm or 101.325 kPa). The gas volume expansion ratio of liquid neon is 1445 to 1. Therefore, any time there is a leak or spill of an inert gas cryogen, there is a serious hazard of oxygen deficiency in the atmosphere. The cold boil-off vapors of these inert gases can generally be seen as fog due to condensing moisture in the air. However, these vapors quickly transform into invisible inert gas at room temperature and extend beyond the visible fog near the spill.

Nonflammable liquefied gases such as carbon dioxide, sulfur hexafluoride, and nitrous oxide also pose the hazard of asphyxiation by reducing the oxygen content in air if large quantities are spilled or released. Carbon dioxide is much heavier than air and can accumulate in low areas replacing oxygen necessary to support life, as can sulfur hexafluoride, which is also much heavier than air. In addition, carbon dioxide in concentrations exceeding the Threshold Limit Value–Time-Weighted Average (TLV–TWA) of 5000 ppm can adversely affect the acid-base balance and other bodily functions. Nitrous oxide, an anesthetic gas, is both heavier than air and is an oxidizer.

A portable SCBA or air-line respirator must be worn by any personnel entering areas containing an oxygen-deficient atmosphere, as defined by OSHA, or in any case where the oxygen concentration in the atmosphere is suspected to be less than 19.5 percent by volume.

Potentially oxygen-deficient atmospheres in confined spaces

Whenever personnel are working in potentially oxygen-deficient atmospheres (as with inert gases), they must be equipped with a portable SCBA or air-line breathing equipment and have a person standing outside of the area to signal if an emergency should occur.

Never enter an area where a potentially oxygen-deficient atmosphere may exist without testing the atmosphere for oxygen content (and any other suspected hazardous products). Tanks, pits, and vessels not designed for occupancy, considered as confined spaces, are of particular concern. Because of the high number of fatal injuries associated with entering these areas, OSHA regulates such workplace activity under Title 29 of the U.S. *Code of Federal Regulations* (29CFR) 1910.146, "Permit-Required Confined Space Entry Standard" [23]. Confined space entry requirements include identifying potential confined spaces, having an entry-permit system, atmospheric testing and monitoring, isolating by lockout/tagout, blanking and disconnecting lines, ventilating the area, providing "hole watches" or observers, securing

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entrants with harnesses or lifelines, having personal protective equipment (PPE) including an air-line SCBA or other respirators, providing rescue personnel services where appropriate, and extensive training for all participants.

More detailed information is available in CGA P-14, *Accident Prevention in Oxygen-Rich and Oxygen-Deficient Atmospheres*, and CGA P-12, [24, 16]. CGA also publishes a brief safety bulletin, CGA SB-2, *Oxygen-Deficient Atmospheres* [25], which emphasizes the potential seriousness of this invisible hazard.

Oxidizers

Oxygen and gas mixtures containing a high percentage of oxygen react chemically with organic materials to produce heat. *This reaction can take place with explosive violence.* Therefore, keep all combustible materials and potential sources of ignition away from oxygen or gas mixtures containing concentrations of oxygen greater than 23.5 percent.

All equipment to be used for oxygen service, whether the oxygen is in a gaseous or liquid state, must be specifically cleaned for oxygen service to remove any traces of oils, greases, or other hydrocarbon materials. Procedures for cleaning components and systems to be used for oxygen service are contained in Chapter 11 and in CGA G-4.1 [17].

Caution: Never permit oil, grease, or other combustible substances to come in contact with cylinders, valves, regulators, gases, hoses, and fittings used for oxidizing gases such as oxygen and nitrous oxide, which may combine with these substances with explosive violence. Never lubricate valves, regulators, gauges, or fittings with oil or any other combustible substance. Do not handle cylinders with oily hands or gloves, and never store cylinders where oil, grease, or other readily combustible substances may come in contact with them.

Caution: Clothing on which liquid oxygen is spilled or clothing exposed to an oxygen-rich atmosphere can pose a serious hazard of fire or explosion due to the rapid chemical reaction between the two substances.

If liquid oxygen is spilled on clothing, the clothing must be removed at once and aired out before reuse. See CGA P-14 for more detailed recommendations regarding clothing that may become exposed to oxygen-rich atmospheres [24]. Areas where liquid oxygen may be spilled during transfer operations must be free of hydrocarbons or other combustible materials. Never transfer liquid oxygen where it may spill onto asphalt surfaces or gravel or another porous material that may contain oil drippings.

Oxidizing gases such as fluorine, chlorine, nitrogen trifluoride, and nitrous oxide are covered in individual gas monographs in Part II.

Poison (toxic) gases

Caution: Poison gases such as arsine, diborane, methyl bromide, nitric oxide, nitrogen dioxide, phosgene, and phosphine pose serious potential hazards to personnel and therefore require special handling.

These products must never be handled except by specially trained personnel who are fully aware of the potential hazards involved and who are equipped with such special personal safety apparatus as is necessary in to handle these products.

Cartridge-type respirators or SCBAs of an approved design are two types used for emergency response purposes. Cartridge-type respirators may be used only where the concentrations of the toxic or poison gas involved will not exceed the rating of the particular cartridge-type respirator used and where the oxygen content of the atmosphere is not less than 19.5 percent by volume. Such equipment must be readily accessible, but kept out of the area most likely to become contaminated. Personnel entering areas with poison (toxic) gases must be highly trained and practiced in handling emergencies involving these products.

Highly toxic or poison gases must be stored in accordance with local building and fire codes. Storage locations must be clearly marked and protected against tampering or entry by unauthorized persons. The total quantity of highly toxic or poison gases stored at a user's site should be limited to foreseeable requirements.

Highly toxic or poison gases should be filled and used only in mechanically ventilated areas, preferably in hoods with forced ventilation.

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Such gases, when emitted from equipment at concentrations above permitted levels, must be discharged into appropriate treatment equipment designed to reduce the concentration of the toxic gases in the effluent gas stream to acceptable levels.

Before using a highly toxic or poison gas, the user should be familiar with all information on the container label and the MSDS associated with the product. All personnel working in the immediate area must be instructed regarding the toxicity of the gases being used, the appropriate methods of protection against harmful exposure, emergency procedures, and first aid treatment in case of exposure. Permissible exposure limits (PELs®), as required by OSHA, for employees handling highly toxic or poisonous gases are expressed in parts per million (ppm) of mixtures of the gas in air or milligrams per cubic meter over a period of 8 hours. PELs are listed in 29 CFR Part 1910 Subpart Z [23]. Information regarding TLVs® is available in the annually updated *Threshold Limit Values (TLVs®) and Biological Exposure Indices (BEIs®),* published by the American Conference of Governmental Industrial Hygienists (ACGIH) [26].

Because of the hazardous nature of highly toxic and poisonous gases, people handling them are advised to contact the supplier for more complete information about use, emergency response measures, and first aid. More detailed information regarding the chemical and physical properties of poison gases, their effects on humans, and safety precautions may be found in the specific gas monographs in Part II.

Corrosive gases

Corrosive gases can be grouped into two categories. The first category is acidic gases, which forms acids upon exposure to water. The second category includes gases that form alkaline materials upon exposure to water.

Examples of acidic gases are boron trichloride, boron trifluoride, chlorine, dichlorosilane, hydrogen bromide, hydrogen chloride (anhydrous), hydrogen fluoride, and sulfur dioxide. Examples of alkaline gases are ammonia, monomethylamine, dimethylamine, and trimethylamine. These gases may exhibit other hazards such as toxicity, oxidization potential, or flammability. The physical and chemical properties of these gases, their physiological effects on humans, special precautions to be followed, and first aid measures are covered in individual gas monographs in Part II.

Precautions must be taken to avoid contact of the skin or eyes with acidic or alkaline gases.

Goggles or face shields and rubber (or other suitably chemically resistant material) gloves and aprons must be worn when handling these products. Open shoes or sneakers must not be worn when handling these products. To be prepared in case of emergency, personnel handling and using acidic or alkaline gases should have cartridge-type respirators or SCBAs of an approved design immediately available.

Areas where acidic or alkaline gases are filled or used should be equipped with an emergency shower and eyewash fountain. Drenching with copious amounts of water is the accepted first aid procedure in the event of exposure to the skin or eyes. Persons accidentally exposed to such gases should receive prompt attention by a physician.

Acidic or alkaline gases should be used only in a well-ventilated area, and quantities stored at a user's site should be limited to those required for foreseeable use.

Pyrophoric gases

Pyrophoric gases such as silane are categorized as spontaneously flammable, meaning they may immediately ignite on contact with air, form explosive mixtures with air, and do not need a source of ignition to burn. They can also be harmful if inhaled.

Containers of pyrophoric gases must be kept away from heat, sparks, and open flames in a well-ventilated area. Spark-resistant tools should be used. Use pyrophoric gases only in a closed system designed to withstand the pressure involved. All equipment should be evacuated or purged with inert gas prior to opening the cylinder valve. Use a check valve or back-flow protection device in any line or piping from the container to prevent reverse flow and potential reaction, which could cause a container failure.

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In case of a leak, shut off product gas flow to be certain that gas has not accumulated to form an explosive mixture and it is safe to do so. Do not extinguish burning gas if product flow cannot be shut off immediately. Use water spray or fog nozzle to keep nearby cylinders cool. Evacuate area in danger and keep personnel upwind.

If gas is inhaled, remove victim to fresh air and provide appropriate medical attention.

DISPOSAL

Environmental regulations may affect cylinder handling and disposal. For example, environmental regulations affect cylinder handling because of the need to properly dispose of some gases upon return for refilling. Likewise, disposal of the porous mass in scrap acetylene cylinders may be subject to environmental regulations. Certain toxic gases must be released only through scrubbers or other safe disposal means, or can be recycled only when suitable quality can be assured. More detailed information regarding EPA regulations can be found in Chapter 3. In Canada, federal and provincial health and safety, environmental, and medical regulations must be met.

TRANSPORTING

Compressed gases and cryogenic liquids in containers pose certain potential hazards when being transported. Containers can leak or be damaged in transport. Hazards can be created from the containers themselves when subject to impact from a vehicle accident, when the container is not properly secured in a vehicle, or when the product being transported is released from its container exposing people or the environment to the hazardous materials.

Since compressed gases and cryogenic liquids are defined as hazardous materials by DOT and TC regulations, the transportation of these products by the gas manufacturers and suppliers is subject to considerable safety-related regulations. Unfortunately many of the more serious incidents leading to injury or fatality have occurred from transporting containers in unsuitable vehicles and in a hazardous manner.

Examples of this are flammable gas containers placed in the trunk of an automobile where a leaking cylinder can result in an explosion. Likewise, a container leak from an inert or asphyxiant gas in a confined area such as the passenger area of a vehicle may result in hypoxia or asphyxiation.

The preferred and safest method of transporting compressed gases and cryogenic containers is to use vehicles designed and equipped for such purposes. A suitable vehicle is one that is adequately ventilated in the event of a product leak, and has an adequate method for securing any cylinders and containers during transport. However, as a minimum, the person(s), whether supplier or customer, transporting a compressed gas container in a vehicle must:

- be knowledgeable of the hazards and precautions for the product(s) transported;
- check any containers for damage or leaks;
- secure the container against movement;
- ensure that valve protection caps and valve outlet plugs or caps are in place;
- make sure the container storage area is well ventilated;
- not allow smoking or open flames within close proximity;
- know what to do in case of a leak, incident, or emergency;
- drive safely obeying all traffic laws and require occupants to wear seat belts; and
- know product-related regulations and supplier instructions.

For additional information see CGA PS-7, *CGA Position Statement on the Safe Transportation of Cylinders in Vehicles* [27].

For other than consumer commodities of hazardous materials or materials of trade (MOTs), the driver of any vehicle picking up and transporting DOT hazardous materials must have a shipping paper and appropriate emergency response information. If more than 1001 pounds of a nonflammable or flammable, nonpoisonous gas are being carried, placards are required to be displayed on the vehicle. (Placards are required when shipping ***any quantity*** of poison or toxic gas.) When a placard is required, the vehicle meets the DOT requirements defining a commercial motor vehicle [28]. This imposes significant requirements including:

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- Driver must possess a valid commercial driver's license (CDL).
- Driver must be participating in a random drug-testing program (49 CFR Part 383).
- Driver qualifications found in 49 CFR Part 391 must be met.

EMERGENCY RESPONSE

Due to the potentially hazardous nature of many compressed gases and cryogenic liquids during manufacture, storage, transport, and use, there is an essential need for effective, informed, and timely emergency response:

- to prevent or minimize injury to persons, or property, or damage to the environment in the event of an incident;
- to facilitate the expeditious handling of any cleanup; and
- to analyze the causes of the incident and the effectiveness of the emergency response so future corrective or preventive measures can be taken.

In 1988, CGA implemented a plan for the industry, entitled the Compressed Gas Emergency Action Plan (COMPGEAP®), which helps to coordinate emergency response activities of member companies during physical distribution activities. The COMPGEAP plan is activated through the Chemical Transportation Emergency Center (CHEMTREC) emergency response network, established by the Chemical Manufacturers Association (CMA), which is designed to speed emergency response information on hazardous materials to sites anywhere within the United States. In Canada, shippers of dangerous goods in quantities above those specified in the TDG Regulations are required to register an Emergency Response Assistance Plan (ERAP) with TC [2]. These plans can be activated by anyone in possession of the shipping document or through Canadian Transport Emergency Centre (CANUTEC), who also acts as a disseminator of information on dangerous goods. In both countries the primary responsibility for emergency response lies with the manufacturer, transporter, or user of the hazardous material(s).

Developing an emergency response plan

For any company manufacturing, storing, handling, or transporting compressed gases or cryogenic liquids, the development and implementation of an emergency response plan must be considered a first priority. Locally within the United States, fire code regulations will be used to develop a Hazardous Materials Management Plan (HMMP) for extremely hazardous substances (EHS). The *Superfund Amendments and Reauthorization Act* (SARA) *Title III*, OSHA Process Safety Management, and Clean Air Act Risk Management Plan all mandate the development of a site-specific emergency response plan. Such a plan must take into consideration the specific hazards associated with the materials being manufactured, stored, or transported, and a thorough analysis of all possible emergency situations that could occur. These events should be analyzed in terms of their probability of occurring and their potential outcomes. Techniques for such analyses can vary from very sophisticated fault-tree analysis to a simple checklist, depending on the level of risk involved.

The types of events that may require an emergency response include:

- storms, floods, hurricanes, tornadoes, and earthquakes;
- accidental release of cryogenic fluids;
- accidental release of flammable, toxic, or corrosive gases;
- fires, power outages, explosions, or bomb threats;
- highway, rail, or other transport incidents;

and any other possible events that could trigger the release of hazardous material into the environment.

When analyzing the probability of emergency events, it is important to recognize that in many cases one type of emergency may often trigger subsequent events that may have even greater

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consequential implications than the initiating event.

Although most written emergency response plans contain the same basic elements, there are two distinct types to consider–plans applicable to a facility or site location, and plans associated with transportation incidents.

On-site emergency response

When developing a facility or site emergency response plan, it is not enough to focus on the effects of possible accidents at the site itself. Also to be considered are the effects on the surrounding community and the need to coordinate emergency response planning with local officials, including police, fire, and medical emergency rescue personnel. In Canada, this process is addressed by standard CAN/CSA Z731, *Emergency Planning for Industry* [29].

As a starting point, a plot plan of the site should be prepared showing the locations of existing structures, property lines, entrances, exits, fire hydrants, sprinkler systems, emergency equipment, plant controls and shutoffs, and areas where specific hazardous materials are handled or stored.

To determine which materials may be hazardous, copies of MSDSs should be obtained and evaluated. Information should be gathered and analyzed regarding the areas immediately adjacent to the site including information on local topography; area classification (residential, industrial, commercial); transportation routes; and available community and emergency services such as police, fire, emergency rescue, and medical services.

Once this has been completed, an analysis should be made of the potential scenarios that might trigger an emergency involving either the site alone or the site and surrounding community.

A written emergency response plan for a site location should include, at a minimum, the following: (Specific regulations, for example, Process Safety Management (PSM) or Risk Management Program (RMP) may require other elements.)

- Evacuation procedures for the site and (if appropriate) the community adjacent to the site
- A list of current emergency numbers to be used to alert plant personnel; and local police, fire, emergency rescue, and medical personnel
- A list of site personnel, including duties and phone numbers for those responsible for implementation of the plan
- A list of types and quantities of hazardous materials including compressed and liquefied gases
- MSDSs detailing the chemical and physical properties of hazardous materials being stored or handled, and specific emergency response measures to be implemented to contain these materials in the event of an emergency
- A detailed plot plan designating areas where hazardous materials are handled or stored
- A list of emergency equipment available and the locations of such equipment.
- A schedule for periodic discussions of the plan with local officials and police, fire, rescue, medical and other emergency response personnel
- A plan for employee training to ensure that all employees understand the emergency response plan and their respective responsibilities in the event of an emergency
- A schedule for implementing periodic fire drills and for testing other emergency response procedures, including evacuation of the site

Transportation emergencies and response

The chief differences between transportation emergencies involving hazardous materials and those occurring at a site involve the greater unpredictability of transportation incidents; the substantial risk of public exposure; and the difficulty of locating, organizing, and coordinating

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the efforts of the resources necessary to bring the incident under control.

It is the product carrier who has the prime responsibility to handle a transportation emergency, although the product shipper, especially in situations where a hazardous material is being transported, usually has the greatest expertise in handling an emergency. Generally the shipper's role is advisory in nature, providing information on product hazards, handling, and cleanup to those at the scene who are responsible for dealing with the emergency.

The first line of defense in handling a transportation emergency is to make sure that the carrier has the basic hazard and other MSDS-type information on the product(s) being transported and knows who to notify in the event of an emergency. DOT and TC require that a 24-hour emergency response number, emergency response information, and other such information be provided to the driver in separate documents or indicated on the driver's hazardous material shipping papers. Vehicles transporting hazardous materials may be placarded to indicate the hazardous nature of the materials being transported as described in Chapter 3 (Placarding).

CHEMTREC (Chemical Transportation Emergency Center) Services

Emergency response assistance in any transportation emergency within the United States involving compressed gases (as well as other chemicals) can be obtained through the CMA's CHEMTREC by calling toll free 800-424-9300. CHEMTREC provides 24-hour-a-day response, 7 days a week, and offers immediate advice for those at the scene of emergencies, then promptly notifies the shipper to receive more detailed assistance and the appropriate follow-up. Shippers of compressed gases are encouraged to register with CHEMTREC.

For further information about CHEMTREC services, write to Manager, CHEMTREC/CHEMNET, Chemical Transportation Emergency Center, Chemical Manufacturers Association, 1300 Wilson Boulevard, Arlington, VA 22209; or phone (703) 741-5000.

CANUTEC (Canadian Transport Emergency Centre, or Centre Canadien D'Urgence Transport)

TC also operates a 24-hour emergency response information service called CANUTEC, which can be reached in emergencies by calling (613) 996-6666. For general information about this service, call (613) 992-4624.

Canadian regulations covering the transportation of dangerous goods require shippers of certain dangerous goods in excess of specific quantities to register an ERAP with TC. The registered number must be shown on any shipment of this material over the specified quantity. In all cases, shipping documents for dangerous goods requiring an ERAP must also provide a phone number through which the plan can be activated at any time during the day.

In Canada, the Canadian Chemical Producers Association (CCPA) operates a mutual aid program for its members, the Transportation Emergency Assistance Plan (TEAP). In addition, the Propane Gas Association of Canada (PGAC) operates a mutual aid response plan for its members. TEAP is designed to handle emergencies involving any member's products, while the PGAC plan deals with incidents involving liquefied petroleum gas.

Further information on these plans can be obtained from the CCPA at 350 Sparks Street, Suite 850, Ottawa, Ontario K1A 7S8, and the PGAC at 500 Fourth Avenue SW, Suite 1202, Calgary, Alberta T2P 2V6.

Emergency response by producers

In addition to the emergency response information available from CHEMTREC and CANUTEC, many shippers of hazardous materials have the capability of dispatching an emergency response team to the site of an incident involving hazardous materials. Such teams are trained and equipped to provide product information and guidance to local emergency personnel and, in many cases, can provide special

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equipment such as acid suits, portable breathing apparatus, containment vessels, portable scrubbers, recovery drums. These teams are capable of making on-site cargo transfers, if necessary. (See Fig. 2-2.)

Implementing the emergency response plan

Once a written emergency response plan has been developed, it must be implemented at all levels throughout the organization through communication and training programs for employees, as well as communication and coordination with local emergency response agencies.

For an emergency response plan to be effective, it is essential that rapport be established with local emergency response agencies, such as fire and police departments and local medical facilities. Meetings should be held with members of these agencies to educate them about the specific hazards defined in the plan and the planned responses to be taken in the event of an emergency. Outside agency representatives should be invited to the site to become familiar with the site layout; the processes and materials involved; the number of employees at the site; the locations and types of emergency equipment available at the site; and the specific properties and hazards associated with any hazardous materials being produced, stored, or used at the site.

Testing the emergency response plan

Because of infrequent emergency response events relative to the large number of shipments or hours of production at facilities, the emergency response plan must be tested periodically to ensure that it will be effective when an emergency arises. All employees and local emergency response personnel must understand their responsibilities in carrying out the plan. Periodic tests of the emergency response plan must take into consideration the frequency of changes in personnel both on-site and in outside agencies.

When such tests are carried out, the occurrence of a particular event should be simulated and all responsible personnel should be required to respond in accordance with the plan. Such

Fig. 2-2. Emergency response team trains for containment of a leaking cylinder using a cylinder containment vessel.

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tests give those in charge of the emergency response program an opportunity to evaluate the effectiveness of the plan, to identify any flaws in the system, and to test the understanding and readiness of personnel assigned to critical responsibilities.

Post emergency activities

After an emergency situation has been brought under control, the next objective should be to implement necessary cleanup operations and get the operation back to normal. At the same time, an investigation should be started to determine the cause(s) of the incident, to identify corrective measures to be taken to prevent future emergencies, and to evaluate the effectiveness of the emergency response effort.

Before initiating these activities, the area where the incident occurred should be secured to prevent the disruption, displacement, or destruction of physical evidence; to ensure that salvageable equipment and materials are not removed; and to prevent unauthorized persons from entering the site and incurring possible injury. In certain instances, photographs taken of the site and specific details of equipment can be useful in reconstructing events and assessing damage. Once this has been done, the physical evidence should be cataloged and removed for further examination.

After the post-emergency investigation has been completed, the results of this investigation, together with any resulting changes or improvements in procedures, equipment, or the emergency response plan, should be communicated to concerned employees and to local emergency response agencies.

Conclusion

Effective emergency response requires a commitment at all levels within an organization starting from the top down. Such response can be effective only when the necessary resources are made available for planning, training, coordination, testing, and implementation.

Often the only positive result that comes from an actual emergency incident is reinforcement of the fact that such incidents can and do happen, and that resources expended on emergency preparedness are a sound investment.

SAFETY TRAINING

Effective safety training is critical to the compressed gas business. The mishandling or misuse of compressed gases, liquefied compressed gases, or cryogenic gases can result in injuries and property damage in dramatic proportions. The potential for human suffering, equipment loss, and environmental damage requires the adoption of a comprehensive loss prevention program incorporating training to avoid and minimize unintended product releases, equipment failures, and human error.

There are many resources available for training materials. Industry associations, such as CGA, technical standards organizations such as the American National Standards Institute (ANSI), and regulatory agencies like OSHA all offer excellent materials to incorporate into an overall training program. These organizations set minimum guidelines, standards, and requirements to help maintain safety in the compressed gas industry.

A good place to start is by reviewing training requirements as set forth by OSHA and other safety-focused regulatory agencies. A compressed gas manufacturer or supplier should be able to offer technical information, such as the physical and chemical properties of the products provided (including MSDS). Information may also be available covering the characteristics of the products, the protective equipment necessary, proper procedures for storage and handling, procedures to minimize the likelihood of accidents, and the corrective measures and emergency procedures to be followed in the event of an incident.

The first step to develop in-house training is to identify training needs. Employees can provide information on training needs by answering questions about job concerns and safety incidents. Other methods include conducting a job hazard/process analysis or other type of analysis

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