

Safetygram #6

Liquid Oxygen

General

Oxygen is the second largest component of the atmosphere, comprising 20.8% by volume. Liquid oxygen is pale blue and extremely cold. Although nonflammable, oxygen is a strong oxidizer. Oxygen is necessary to support life.

Oxygen will react with nearly all organic materials and metals, usually forming an oxide. Materials that burn in air will burn more vigorously in oxygen. Equipment used in oxygen service must meet stringent cleaning requirements, and systems must be constructed of materials that have high ignition temperatures and that are nonreactive with oxygen under the service conditions. Vessels should be manufactured to American Society of Mechanical Engineers (ASME) codes and designed to withstand the process temperatures and pressures.

Liquid oxygen is a cryogenic liquid. Cryogenic liquids are liquefied gases that have a normal boiling point below -238°F (-150°C). Liquid oxygen has a boiling point of -297.3°F (-183.0°C).

Because the temperature difference between the product and the surrounding environment is substantial—even in the winter—keeping liquid oxygen insulated from the surrounding heat is essential. The product also requires special equipment for handling and storage.

Oxygen is often stored as a liquid, although it is used primarily as a gas. Liquid storage is less bulky and less costly than the equivalent capacity of high-pressure gaseous storage. A typical storage system consists of a cryogenic storage tank, one or more vaporizers and a pressure control system. The cryogenic tank is constructed, in principle, like a vacuum bottle. There is an inner vessel surrounded by an outer vessel. Between the vessels is an annular space that contains an insulating

medium, from which all the air has been removed. This space keeps heat away from the liquid oxygen held in the inner vessel. Vaporizers convert the liquid oxygen into a gaseous state. A pressure control manifold then controls the gas pressure that is fed to the process or application.

Vessels used in liquid oxygen service should be designed according to ASME codes for the pressure and temperatures involved. Piping design should follow similar codes, as issued by the American National Standards Institute (ANSI).

Manufacture

Oxygen is produced by an air separation unit (ASU) through liquefaction of atmospheric air and separation of the oxygen by continuous cryogenic distillation. The oxygen is then removed and stored as a cryogenic liquid. Oxygen can also be produced noncryogenically using selective adsorption processes to produce gaseous product.

The ASU manufacturing process begins with a main air compressor and ends at the output of the product storage tanks. Air is compressed and sent through a cleanup system where moisture, carbon dioxide, and hydrocarbons are removed. The air then passes through heat exchangers where it is cooled to cryogenic temperature. Next, the air enters a high pressure distillation column where it is physically separated into a vaporous form of nitrogen at the top of the column and a liquid form of “crude” oxygen ($\sim 90\% \text{O}_2$) at the bottom.

This crude oxygen liquid is withdrawn from the column and sent to a low-pressure column, where it is distilled until it meets commercial specifications. The liquid oxygen is sent to a cryogenic storage tank.

Uses

Oxygen is generally liquefied so that it can be more effectively transported and stored in large volumes. However, most applications use oxygen after it is vaporized to the gaseous form. The primary uses of oxygen relate to its strong oxidizing and life-sustaining properties. Oxygen is commonly relied upon in health and medical applications. Liquid oxygen is used as an oxidant for liquid fuels in the propellant systems of missiles and rockets.

Oxygen is widely applied in the metal industries in conjunction with acetylene and other fuel gases for metal cutting, welding, scarfing, hardening, cleaning and melting. Steel and iron manufacturers also extensively use oxygen or oxygen-enriched air to affect chemical refining and heating associated with carbon removal and other oxidation reactions. Benefits such as fuel and energy savings plus lower total emission volumes are often achieved when air is enriched or replaced with higher-purity oxygen.

In the chemical and petroleum industries, oxygen is used as a feed component to react with hydrocarbon building blocks to produce chemicals such as alcohols and aldehydes. In many processes, the oxygen for reaction can be obtained from the use of air. However, direct use of oxygen, or enrichment of the air with oxygen, is necessary for some processes. There are several major petrochemical intermediates that are presently manufactured with high-purity oxygen, including ethylene and propylene oxide (antifreeze), vinyl chloride (for PVC), and caprolactam (for nylon).

The pulp and paper industry uses oxygen as a bleaching and oxidizing agent. A variety of process (liquor) streams show enhanced physical properties after treatment with oxygen; plant operating costs also improve.

Similarly, oxygen enhances the combustion process in industries that manufacture glass, aluminum, copper, gold, lead, and cement, or that are involved in waste incineration or remediation. There are corresponding productivity, energy, maintenance, and emissions benefits end users may realize.

Wastewater treatment plants successfully employ oxygen to enhance their chemical process efficiency. Aquaculturists such as fish-farmers also see benefits in the health or size of their livestock when the host environment is oxygenated.

Table 1

Liquid Oxygen Physical and Chemical Properties

Molecular Formula	O ₂
Molecular Weight	31.999
Boiling Point @ 1 atm	-297.4°F (-183.0°C)
Freezing Point @ 1 atm	-361.9°F (-218.8°C)
Critical Temperature	-181.8°F (-118.4°C)
Critical Pressure	729.1 psia (49.6 atm)
Density, Liquid @ BP, 1 atm	71.23 lb/scf
Density, Gas @ 68°F (20°C), 1 atm	0.0831 lb/scf
Specific Gravity, Gas (air=1) @ 68°F (20°C), 1 atm	1.11
Specific Gravity, Liquid (water=1) @ 68°F (20°C), 1 atm	1.14
Specific Volume @ 68°F (20°C), 1 atm	12.08 scf/lb
Latent Heat of Vaporization	2,934 Btu/lb mole
Expansion Ratio, Liquid to Gas, BP to 68°F (20°C)	1 to 860
Solubility in Water @ 77°F (25°C), 1 atm	3.16% by volume

Health Effects

Normally air contains 21% oxygen and oxygen is essentially nontoxic. No health effects have been observed in people exposed to concentrations up to 50% at 1 atmosphere for 24 hours or longer.

The inhalation at 1 atmosphere of 80% oxygen for more than 12 hours can cause irritation of the respiratory tract, progressive decrease in vital capacity, coughing, nasal stuffiness, sore throat, and chest pain, followed by tracheobronchitis and later by pulmonary congestion and/or edema.

Inhalation of pure oxygen at atmospheric pressure or less can cause pulmonary irritation and edema after 24 hours.

Respiratory symptoms can occur in two to six hours at pressures above 1 atmosphere. One of the earliest responses of the lung is accumulation of water in its interstitial spaces and within the pulmonary cells. This can cause reduced lung function, which is the earliest measurable sign of toxicity. Other symptoms include fever, and sinus and eye irritation.

When pure oxygen is inhaled at pressures greater than 2 or 3 atmospheres, a characteristic neurological syndrome can be observed. Signs and symptoms include nausea, dizziness, vomiting, tiredness, light-headedness, mood changes, euphoria, confusion, incoordination, muscular twitching, burning/tingling sensations (particularly

of the fingers and toes), and loss of consciousness. Characteristic epileptic-like convulsions, which may be preceded by visual disturbances, such as loss of peripheral vision, also occur. Continued exposure can cause severe convulsions that can lead to death. The effects are reversible after reduction of oxygen pressure.

Premature infants placed in incubators to breathe oxygen in concentrations greater than in air can develop irreversible eye damage. Within six hours after an infant is placed in a high-oxygen atmosphere, vasoconstriction of the immature vessels of the retina occurs, which is reversible if the child is immediately returned to air, but irreversible if oxygen-rich therapy is continued. Fully developed blood vessels are not sensitive to oxygen toxicity.

Extensive tissue damage or cryogenic burns can result from exposure to liquid oxygen or cold oxygen vapors.

Containers

Liquid oxygen is stored, shipped, and handled in several types of containers, depending upon the quantity required by the user. The types of containers in use include the dewar, cryogenic liquid cylinder, and cryogenic storage tank. Storage quantities vary from a few liters to many thousands of gallons. Since heat leak is always present, vaporization takes place continuously. Rates of vaporization vary depending on the design of the container and the volume of stored product.

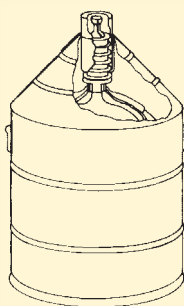
Containers are designed and manufactured according to the applicable codes and specifications for the temperatures and pressures involved.

Dewars

Figure 1 illustrates a typical, vacuum-jacketed dewar. A loose-fitting dust cap over the outlet of the neck tubes prevents atmospheric moisture from plugging the neck and allows gas produced from vaporized liquid to escape. This type of container is non-pressurized. The most common unit of measure for the capacity of a dewar is the liter. Five- to 200-liter dewars are available. Product may be removed from small dewars by pouring, while larger sizes will require a transfer tube. Cryogenic liquid cylinders which are pressurized vessels are sometimes incorrectly referred to as dewars.

Figure 1

Typical Dewar



Cryogenic Liquid Cylinders

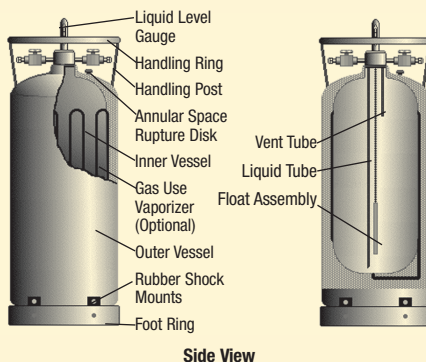
A typical cryogenic liquid cylinder is depicted in Figure 2. This is an insulated, vacuum-jacketed, pressure vessel. They are equipped with pressure-relief valves and rupture disks to protect the cylinders from pressure buildup. Liquid containers operate at pressures up to 350 psig and have capacities between 80 and 450 liters of liquid. Oxygen may be withdrawn as a gas by passing liquid through an internal vaporizer or as a liquid under its own vapor pressure. For more details on the construction and operation of cryogenic liquid cylinders, consult Air Products' Safetygram #27, "Cryogenic Liquid Containers."

Cryogenic Storage Tanks

Customer installations generally include a tank, vaporizer, and pressure control manifold (see Figure 3). Tanks may be spherical or cylindrical in shape and are mounted in fixed locations as stationary vessels or on railcar or truck chassis for easy transportation. Sizes range from 500 to 420,000 gallons. All tanks are powder and vacuum insulated in the annular space and equipped with various circuits to control product fill, pressure

Figure 2a

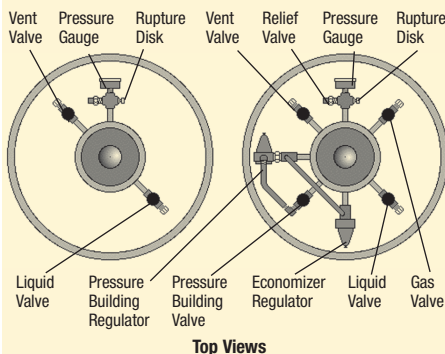
Typical Cryogenic Liquid Cylinder, side view



Side View

Figure 2b

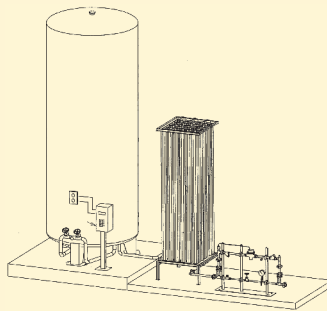
Typical Cryogenic Liquid Cylinder, top view



Top Views

Figure 3

A Typical Customer Station with a Cryogenic Storage Tank



build-up, pressure-relief, product withdrawal, and tank vacuum. Tanks are designed to ASME specifications for the pressures and temperatures involved.

Transfer Lines

A liquid transfer line is used to safely remove liquid product from dewars or cryogenic liquid cylinders. A typical transfer line for dewars is connected to

a bayonet that provides a means of using product vapor pressure buildup or an external pressure source to remove the liquid. For cryogenic liquid cylinders, the transfer line is connected to the cylinder's liquid withdrawal valve.

Liquid product is typically removed through insulated withdrawal lines to minimize the loss of liquid product to gas. Insulated flexible or rigid lines are used to withdraw product from storage tanks. Connections on the lines and tanks vary by manufacturer.

NOTE: Liquid cylinders designed to dispense gaseous oxygen have valves equipped with standard Compressed Gas Association (CGA) outlets. Suitable pressure-regulating equipment may be attached. Valves provided for the withdrawal of liquid product are also equipped with standard CGA outlets but differ from connections used for gaseous withdrawal. This prevents cross connections between processes using the liquid or gaseous product.

Shipment of Liquid Oxygen

All shipments of liquid oxygen must comply with DOT regulations. This applies to motor freight, rail, air, and water shipments. For air shipments, all packages must also comply with International Air Transport Association/ International Civil Air Organization (IATA/ICAO)

Dangerous Goods regulations: Water vessel shipments must also be prepared in accordance with the International Maritime Organization (IMO) regulations. All packaging used to transport oxygen must be either "UN/DOT Specification" or "UN/DOT Authorized" and in proper condition for transport.

Containers used for transporting liquid oxygen at less than 25 psig (40 psia) pressure are UN/DOT Authorized containers. These are containers built to other than DOT specifications, but ones authorized by DOT for use in the transport of approved products. Containers used for transporting liquid oxygen at pressures greater than 25 psig (40 psia) need to be designed, manufactured, and tested to DOT specifications. DOT Code of Federal Regulations, Title 49 specifies these labeling and identification requirements:

DOT Hazard Class: 2.2

DOT Shipping Label: Nonflammable Gas and Oxidizer (For domestic shipments, only the oxygen label may be used)

Identification Number: UN1073

DOT Shipping Name: Oxygen, Refrigerated Liquid

Placard: Nonflammable Gas

Figure 4

Oxygen Shipping Label



Safety Considerations

The hazards associated with liquid oxygen are exposure to cold temperatures that can cause severe burns; overpressurization due to expansion of small amounts of liquid into large volumes of gas in inadequately vented equipment; oxygen enrichment of the surrounding atmosphere; and the possibility of a combustion reaction if the oxygen is permitted to contact a noncompatible material.

The low temperature of liquid oxygen and the vapors it releases not only pose a serious burn hazard to human tissue, but can also cause many materials of construction to lose their strength and become brittle enough to shatter.

The large expansion ratio of liquid-to-gas can rapidly build pressure in systems where liquid can be trapped. This necessitates that these areas be identified and protected with pressure relief. This expansion ratio also allows atmospheres of oxygen-enriched air to form in the area surrounding a release. It is important to note that fire chemistry starts to change when the concentration of oxygen increases to as little as 23%. Materials easily ignited in air not only become more susceptible to ignition, but also burn with added violence in the presence of oxygen. These materials include clothing and hair, which have air spaces that readily trap the oxygen. Oxygen levels of 23% can be reached very quickly and all personnel must be aware of the hazard.

Any clothing that has been splashed or soaked with liquid oxygen or exposed to high oxygen concentrations should be removed immediately and aired for at least an hour. Personnel should stay in a well-ventilated area and avoid any source of ignition until their clothing is completely free of any excess oxygen. Clothing saturated with oxygen is readily ignitable and will burn vigorously.

Do not permit smoking or open flames in any areas where liquid oxygen is stored or handled. Do not permit liquid oxygen or oxygen-enriched air to come in contact with organic materials or flammable or combustible substances of any kind. Some of the organic materials that can react violently with oxygen when ignited by a spark or even a mechanical shock are oil, grease, asphalt, kerosene, cloth, tar, and dirt that may contain oil or grease. If liquid oxygen spills on asphalt or other surfaces contaminated with combustibles, do not walk on or roll equipment over the area of the spill. Keep sources of ignition away for 30 minutes after all frost or fog has disappeared.

Systems used in oxygen service must meet stringent cleaning requirements to eliminate any incompatible contaminants. The CGA's Pamphlet G-4.1, "Cleaning Equipment for Oxygen Service," describes cleaning methods for equipment used in oxygen service. CGA's Pamphlet O2-DIR, "Directory of Cleaning Agents for Oxygen Service," provides comparative information on cleaning agents used to clean oxygen equipment.

Also, review the Material Safety Data Sheet (MSDS) and follow all recommendations.

Buildings

Because of the large expansion ratio of liquid-to-gas, it is very important to provide adequate ventilation in areas where liquid oxygen is in use. A minimum of six air changes per hour is suggested. CGA has established the definition of an oxygen-enriched atmosphere as one containing at least 23% oxygen.

Remember, oxygen has no warning properties!

Storage

- Store and use liquid containers with adequate ventilation. Do not store containers in a confined area or in area unprotected from the extremes of weather.
- Cryogenic containers are equipped with pressure relief devices designed to control the internal pressure. Under normal conditions these containers will periodically vent product. Do not plug, remove or tamper with any pressure relief device.
- Oxygen must be separated from flammables and combustibles by at least 20 feet or a half-hour fire wall. Post "No Smoking" and "No Open Flames" signs.
- Customer storage sites having a capacity of more than 20,000 scf must be installed in accordance with the National Fire Protection Association (NFPA) Standard 50.

- Liquid containers should not be left open to the atmosphere for extended periods. Keep all valves closed and outlet caps in place when not in use. If restriction results from freezing moisture or foreign material present in openings and vents contact the vendor for instructions. Restrictions and blockages may result in dangerous over-pressurization. Do not attempt to remove the restriction without proper instructions. If possible move the cylinder to a remote location.

Handling

- Cryogenic containers must be stored, handled and transported in the upright position. When moving never tip, slide or roll containers on their side. Use a suitable hand truck for moving smaller containers. Move larger containers by pushing, not pulling. Avoid mechanical and thermal shock.
- Never allow any unprotected part of the body to come in contact with uninsulated pipes or equipment containing cryogenic product. The extreme cold will cause flesh to stick fast and potentially tear on withdrawal.
- Use only oxygen compatible materials and lubricants.
- If there is any difficulty in operating the container valve or container connections discontinue use and contact the vendor. Do not remove or interchange connections. Use only the properly assigned connections.
Do not use adaptors.
- Use only transfer lines and equipment designed for use with cryogenic liquids. Some elastomers and metals, such as carbon steel, may become brittle at extremely low temperatures and may easily fracture. These materials must be avoided in cryogenic service.
- It is recommended that all vents be piped to the exterior of the building.
- On gas withdrawal systems use check valves or other protective apparatus to prevent reverse flow into the container.
- On liquid systems pressure relief devices must be used in lines where there is the potential to trap liquid between valves.

For additional information on the storage and handling of cryogenic liquids refer to Air Products' Safetygram-16, "Safe Handling of Cryogenic Liquids", and CGA Pamphlet P-12, "The Safe Handling of Cryogenic Liquids".

Personal Protective Equipment (PPE)

Personnel must be thoroughly familiar with properties and safety considerations before being allowed to handle liquid oxygen and its associated equipment.

The eyes are the most susceptible to the extreme cold of the liquid and vapors of liquid oxygen. The recommended PPE is a full faceshield over safety glasses; clean, loose-fitting, thermal-insulated or leather gloves; long-sleeved shirts; and pants without cuffs. Wear this PPE when handling or using liquid oxygen, or whenever the possibility of exposure due to a spill exists. In addition, safety shoes are recommended for those involved with the handling of containers.

In emergency situations, self-contained breathing apparatus (SCBA) must be used. Clothing which is fire-resistant in air may be readily ignitable in oxygen-enriched atmospheres. Only trained and certified emergency responders should respond to emergency situations.

First Aid

For skin contact with liquid oxygen, remove any clothing that may restrict circulation to the frozen area. Do not rub frozen parts as tissue damage may result. As soon as practical, place the affected area in a warm water bath with a temperature not exceeding 105°F (40°C). Never use dry heat. Call a physician as soon as possible. Frozen tissue is painless and appears waxy with a possible yellow color. It will become swollen, painful, and prone to infection when thawed. If the frozen part of the body has been thawed, cover the area with a dry sterile dressing with a large bulky protective covering, pending medical care. In case of massive exposure, remove clothing while showering the victim with warm water. Call a physician immediately.

If the eyes are exposed to the extreme cold of the liquid or vapors, immediately warm the frostbite area with warm water not exceeding 105°F (40°C) and seek medical attention.

Fighting Fires

Since oxygen is nonflammable but supports combustion, fire-fighting actions require shutting off the source of oxygen, if possible, then fighting the fire according to the material involved.

Caution: Do not direct water streams toward venting oxygen. The water will freeze and plug the pressure-relief vent, which may result in container failure.

Emergency Response System

- Call: +1-800-523-9374
(Continental U.S. and Puerto Rico)
- Call: +1-610-481-7711 (other locations)
- 24 hours a day, 7 days a week
- For assistance involving Air Products and Chemicals, Inc. products

Product Safety Information

- For MSDS, Safetygrams, and Product Safety Information
www.airproducts.com/productsafety

Technical Information Center

- Call: +1-800-752-1597 (U.S.)
- Call: +1-610-481-8565 (other locations)
- Monday–Friday, 8:00 a.m.–5:00 p.m. EST
- Fax: +1-610-481-8690
- E-mail: gastech@airproducts.com

Information Sources

- Compressed Gas Association (CGA)
www.cganet.com
- American Chemistry Council
www.americanchemistry.com

For More Information

Corporate Headquarters
Air Products and Chemicals, Inc.
7201 Hamilton Boulevard
Allentown, PA 18195-1501

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