



CRYO-STORAGE AND TECHNOLOGIES (CST)

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SafetyAlert-18

Carbon Dioxide

General

Carbon dioxide is nonflammable, colorless, and odorless in the gaseous and liquid states. The gas is approximately one and one-half times as heavy as air. Carbon dioxide is a minor but important constituent of the atmosphere, averaging about 0.03% or 300 ppm by volume. Since dry carbon dioxide is a relatively inert gas, special materials of construction are not required. In the event moisture is present in high concentrations, carbonic acid may be formed and materials resistant to this acid should be used. High flow rates or rapid depressurization of a system can cause temperatures approaching the sublimation point (-109.3°F [-78.5°C]) to be attained within the system. Carbon dioxide will convert directly from a liquid to a solid if the liquid is depressurized below 76 psia (61 psig). The use of materials which become brittle at low temperatures should be avoided in applications where temperatures less than -20°F (-29°C) are expected. Vessels and piping used in carbon dioxide service should be designed to the American Society of Mechanical Engineers (ASME) or Department of Transportation (DOT) codes for the pressures and temperatures involved.

Carbon dioxide can be stored as a bulk liquid in large storage vessels with capacities up to 50 tons and larger. The liquid in the tank is maintained between 245 psig and 305 psig. When the tank pressure reaches 305 psig, a mechanical air-cooled refrigeration unit is activated which cools the tank contents and thereby reduces the pressure to about 295 psig. When pressure drops to 245 psig, a portion of the liquid is passed through a pressure buildup coil which vaporizes the liquid in the coil, and the resultant vapor is sent to the tank's vapor space until a tank pressure of 255 psig is attained. In isolated instances where carbon dioxide usage is extremely low, heat leak into the tank is sufficient to maintain the contents above 245 psig and a pressure buildup coil is not needed. The bulk storage tank can either supply gas from the vapor space or liquid from the bottom of the tank. If warmer carbon dioxide gas is desired, vapor is withdrawn from the vapor space in the storage tank and superheated. Bulk storage tanks are filled by liquid transport trailers.

Carbon dioxide is also pumped as a liquid into high-pressure cylinders which are filled by weight. The amount of carbon dioxide gas contained in a cylinder is determined by multiplying the weight of the liquid by the specific volume at 68°F (20°C) and 1 atmosphere pressure, (8.70 cu. ft./lb.). The vapor pressure of the liquid stored in the cylinder @ 68°F (20°C) is 816 pounds per square inch gauge (psig). Cylinders can be supplied with standard valves for gas withdrawal or with siphon tubes connected internally to the valves for liquid withdrawal.

Carbon dioxide is also stored and shipped as a liquid in cryogenic cylinders at reduced temperature and at a pressure of about 300 psig.

The molecular symbol for carbon dioxide is CO₂.

Toxicity

Carbon dioxide does not support life and may produce immediately hazardous atmospheres. At concentrations in excess of 1.5%, carbon dioxide may produce hyperventilation, headaches, visual disturbances, tremor, loss of consciousness, and death. Symptoms of exposure in the concentration ranges of 1.5-5% may be highly variable but typical symptoms of carbon dioxide intoxication are listed under Exposure Reactions.

If the concentration of carbon dioxide exceeds 10%, exposure may produce profound metabolic aberrations, disturbances of the central nervous system, and cardiac irritability; unconsciousness can occur without warning, preventing self-rescue. At much higher concentrations, carbon dioxide displaces the oxygen in air below levels necessary to support life.

Exposure Limit

The TLV-TWA for CO₂, as listed by American Conference of Governmental Industrial Hygienists and by the Occupational Safety and Health Administration, is 5000 parts per million, or 0.5%. The CAS # for CO₂ is 124-38-9.

Threshold Limit Value-Time Weighted Average (TLV-TWA) is the time-weighted average concentration for a normal 8-hour workday and 40-hour work week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.



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Manufacture

Carbon dioxide is produced as a crude by-product of a number of manufacturing processes. Carbon dioxide is a by-product of steam reforming of methane, propane, or naphtha. The fermentation of sugar to alcohol and the production of lime and sodium phosphate also generate carbon dioxide. Additionally, carbon dioxide exists in natural wells. Once the product has been isolated, impurities are filtered out, moisture is removed in driers, and the purified carbon dioxide is compressed for liquefaction.

Uses

Liquid carbon dioxide is used widely in the food industry for freezing meats, poultry, vegetables, and fruits. Solid carbon dioxide (dry ice) is used to cool meats prior to grinding and also to refrigerate meat and poultry during transit. Soft drinks, wines, and beers are produced using gaseous carbon dioxide for carbonation. Carbon dioxide is used in water treatment to neutralize alkaline water. Liquid carbon dioxide is also used to increase recovery from oil and gas wells. Other industrial uses include the production of chemicals, plastics, rubber, metals, and electronic components.

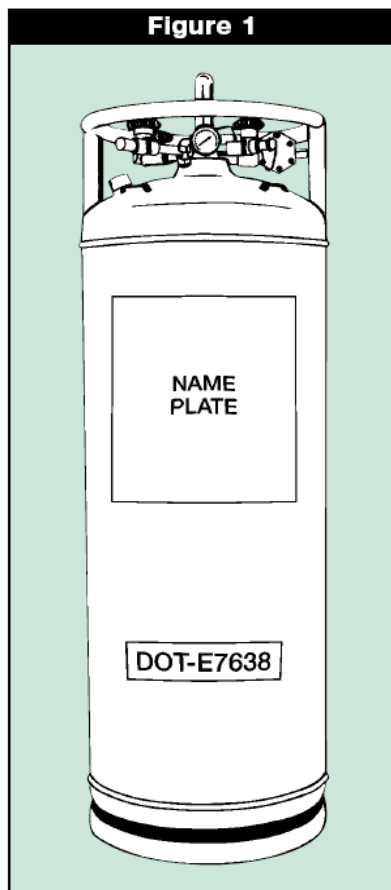
Containers

Bulk carbon dioxide is typically stored as a liquid in storage tanks with capacities of 6, 14, 26, and 50 tons. Tanks are insulated by polyurethane foam with a vapor barrier which provides weather protection. The tanks are fabricated from carbon steel according to ASME Standards. Carbon dioxide is maintained below 305 psig by a refrigeration unit and above 245 psig with a pressure buildup coil so that carbon dioxide can be stored for an indefinite period without venting. Smaller liquid quantities are stored and shipped in cryogenic liquid cylinders with a capacity of 384 pounds (3352 standard cubic feet). Cryogenic liquid cylinders

Properties

Molecular Weight	44.01
Boiling Point @ 1 atm (sublimes)	-109.3°F (-78.5°C)
Freezing Point @ 76 psia	-69.9°F (-56.6°C)
Critical Temperature	87.9°F (31.0°C)
Critical Pressure	1070 psia (72.9 atm)
Density, Liquid @ -35°F (-37°C), 11 atm	68.74 lb./cu.ft.
Density, Gas @ 68°F (20°C), 1 atm	0.115 lb./cu.ft.
Density, Solid @ -110°F (-79°C), 1 atm	97.4 lb./cu.ft.
Specific Gravity, Gas (Air=1) @ 68°F (20°C), 1 atm	1.53
Specific Gravity, Liquid @ -35°F (-37°C), 11 atm	1.10
Specific Volume @ 68°F (20°C), 1 atm	8.70 cu. ft./lb.
Latent Heat of Sublimation	10900 Btu/lb. mole
Solubility in Water @ 68°F (20°C), 1 atm	87.8% by volume

are vacuum-jacketed and can hold product for long periods without venting. Cryogenic liquid cylinders can either supply liquid or gas and liquid. A typical cryogenic liquid cylinder is illustrated in Figure 1.

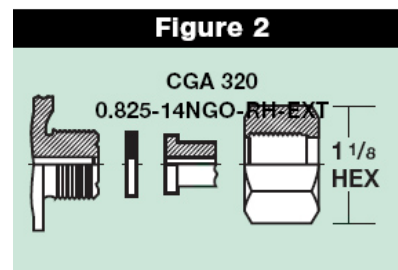


Carbon dioxide is shipped and stored as a liquefied compressed gas in hollow steel and aluminum cylinders. The cylinders have a concave base which allows the cylinders to stand upright and are tapered to a small opening on the top. The tapered or

open end is threaded to receive a cylinder valve or other suitable outlet connection, Safety relief devices are part of the cylinder valve or the outlet connections. A threaded neckring is secured to the tapered end of the cylinder to allow a protective cylinder cap to be installed. Cylinders are manufactured according to Department of Transportation (DOT) specifications. Cylinders in carbon dioxide service are hydrostatically tested upon manufacture, and every five years thereafter at 5/3 times the service pressure.

Gas Cylinder Valves

The Compressed Gas Association and the American National Standards Institute have adopted a thread size of 0.825 inch—14 external right-hand threads per inch—designated as valve connection No. 320 for cylinders. This fitting incorporates a flat nipple and fiber washer for making the gas-tight seal. See Figure 2. For additional information on cylinder valves, request CST SafetyAlert-23: Cylinder Valves.



Safety Devices

Bulk liquid storage tanks are protected against excessive pressures, which may result from heat leak, by reseatable relief devices. Cryogenic liquid cylinders are equipped with reseatable devices and are additionally protected with burst discs. Gas

cylinders are protected from rupture due to fire by a frangible disc sometimes backed by a fusible metal with a melting temperature of about 212°F (100°C).

Identification: Gas Cylinders

Each cylinder is identified between the neckring and shoulder by:

1. The DOT specifications (3A, 3AA, etc.) controlling the manufacture of the container, followed by the service pressure rating in pounds per square inch.
2. Serial number of the container.
3. Manufacturer's symbol and the owner's symbol.
4. Month and year of the container manufacture.
5. Month and year of subsequent 5-year retest of the container.
6. Original inspector's identification stamp.

The neckring usually is identified by the owner's symbol or name.

Identification: Cryogenic Liquid Cylinders

Each cryogenic liquid cylinder is identified with the following information stamped permanently on the shoulder or top head of the jacket, on a permanently attached plate, or on the head protective ring.

1. DOT-4L followed by the service pressure rating in pounds per square inch.
2. Serial number and identifying symbol; location of the number to be just below or immediately following the DOT mark; location of the symbol to be just below or immediately following the number.
3. Month and year of the container manufacture.

Exposure Reactions	
Concentration	Effect
1%	Slight increase in breathing rate
2%	Breathing rate increases to 50% above normal level. Prolonged exposure can cause headache, tiredness.
3%	Breathing increases to twice normal rate and becomes labored. Weak narcotic effect. Impaired hearing, headache, increase in blood pressure and pulse rate.
4-5%	Breathing increases to approximately four times normal rate; symptoms of intoxication become evident and slight choking may be felt
5-10%	Characteristic sharp odor noticeable. Very labored breathing, headache, visual impairment, and ringing in the ears. Judgment may be impaired, followed within minutes by loss of consciousness.
50-100%	Unconsciousness occurs more rapidly above 10% level. Prolonged exposure to high concentrations may eventually result in death from asphyxiation.

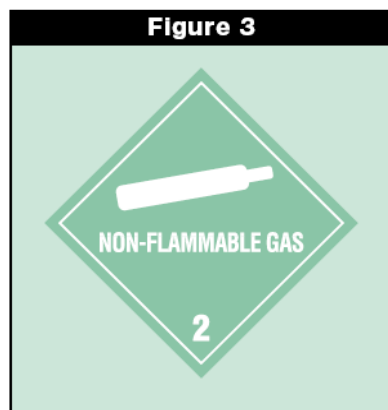
Shipment of Carbon Dioxide: Bulk

Carbon dioxide is transported to bulk supply systems by insulated liquid tankers which must conform to DOT Regulations as set forth in the Code of Federal Regulations, Title 49.

DOT 10³/₄" x 10³/₄" nonflammable gas placards are required on the trailer.

Shipment of Carbon Dioxide: Cylinders

The shipment of carbon dioxide gas cylinders by surface transportation must conform to DOT Regulations, Title 49, which describes labeling and identification required. A DOT 4" x 4" nonflammable gas label or tag is required for common carrier shipments. Figure 3 illustrates the label (black printing on green) that is required.



Cryogenic liquid carbon dioxide cylinders are shipped under DOT Exemption Number 7638. A copy of this exemption must be carried aboard each vessel, aircraft, or motor vehicle used to transport the cylinders. Each cryogenic cylinder must be plainly marked on both sides near the middle, in letters at least two inches high on a contrasting background, "DOT-E 7638." The DOT 4" x 4" green nonflammable gas label or tag is also required for common carrier shipments.

Shipments by air must conform with Title 49 Code of Federal Regulations (FAA Regulations). The official publication of the Department of Transportation concerning transport of hazardous materials by any mode is 49 CFR.

Safety Considerations

Carbon dioxide is stored and transported as a liquefied compressed gas. The following hazards are associated with liquefied compressed carbon dioxide.

1. High pressure involved in storage and service equipment.
2. Carbon dioxide is 1.5 times heavier than air and will not readily disperse in the atmosphere. Asphyxiation may be a hazard in confined areas.
3. Carbon dioxide in high concentrations is toxic to humans. See the toxicity section for effects on humans.
4. Vaporizing carbon dioxide can produce very cold temperatures. Spillage of liquid carbon dioxide on the skin can cause

freeze burn or frostbite. Carbon dioxide, solid below 61 psig, is very cold and sublimates so quickly that prolonged contact with the skin causes freeze burn or frostbite.

Buildings

1. Provide adequate ventilation.
2. The atmosphere in areas in which carbon dioxide gas may be vented and collect should be tested with a portable or continuous monitoring carbon dioxide gas analyzer to ensure ventilation is adequate.

Handling and Storage

1. Never drop cylinders or permit them to strike each other violently.
2. Cylinders should be assigned a definite area for storage. The area should be dry, cool, and well ventilated, and preferably fire-resistant. Keep cylinders protected from excessive temperatures by storing them away from radiators or other sources of heat.
3. Cylinders may be stored in the open, but in such cases should be protected against extremes of weather and from damp ground to prevent rusting.
4. The valve protection cap should be left in place until the cylinder has been secured against a wall, a bench, or placed in a cylinder stand, and is ready to be used.
5. Avoid dragging or sliding cylinders, even for short distances. Cylinders should be moved by a suitable hand truck.
6. Do not use cylinders as rollers for moving material or other equipment.
7. Never tamper with safety devices in valves or cylinders.

8. When returning empty cylinders, close the valve before shipment. Leave some positive pressure in the cylinder. Replace any valve outlet and protective caps originally shipped with the cylinder. Mark and label the cylinder EMPTY. Do not store full and empty cylinders together.

9. No part of a cylinder should be subjected to a temperature above 125°F (52°C). Prevent sparks or flames from welding or cutting torches or any other source from coming in contact with cylinders. Do not permit cylinders to come in contact with electrical apparatus or circuits.

10. Use regulators and pressure relief devices when connecting cylinders to circuits having lower pressure service ratings.

11. Use check valves or traps to prevent backflow of water or other contaminants if backflow can occur into the cylinder. If backflow occurs, mark the cylinder **CONTAMINATED**. Notify the supplier immediately.

12. Provide a safety relief valve on any part of a system where liquid can be trapped between closed valves in lines or vessels.

13. Always keep liquid cylinders upright. Hand trucks are recommended for moving empty and full containers. Containers may be "end-walked" but should never be rolled using the liquid level gauge housing as a pivot point.

14. Know and understand the properties, uses, and safety precautions for carbon dioxide before using the gas and/or associated equipment.

15. Always open a carbon dioxide cylinder valve slowly.

16. If a cylinder protective cap is extremely difficult to remove, do not apply excessive force or pry the cap loose with a bar inserted into the ventilation openings. Attach a label or tag to the

cylinder, identifying the problem and return the cylinder to the supplier.

17. Wrenches should not be used on valves equipped with a handwheel. If the valve is faulty, attach a label or tag to the cylinder identifying the problem and return the cylinder to the supplier.

18. Compressed gas cylinders should not be refilled except by qualified producers of compressed gases.

19. Shipment of a compressed gas cylinder filled without the consent of the owner is a violation of Federal Law.

Personnel Equipment

Safety glasses and shoes and work gloves are recommended when handling high-pressure cylinders. Safety glasses should be worn in areas where vapors are discharged. Use loose-fitting gloves of material that will offer protection, such as leather, when working with cold liquid or vapor.

Use a self-contained breathing apparatus in oxygen-deficient atmospheres or where the carbon dioxide concentration exceeds 1.5%.

First Aid

Persons suffering from the toxic effects of carbon dioxide should be moved to areas with a normal atmosphere. **SELF-CONTAINED BREATHING APPARATUS MAY BE NECESSARY TO PREVENT TOXIC EXPOSURE OR ASPHYXIATION OF RESCUE WORKERS.** Assisted respiration and supplemental oxygen should be given if the victim is not breathing. Frozen tissues should be flooded or soaked with tepid water (not to exceed 107°F [(42°C)]). **DO NOT USE HOT WATER.** Cryogenic burns which result in blistering or deeper tissue freezing should be seen promptly by a physician.

Fire Fighting

Carbon dioxide is nonflammable and is an extinguishing agent for Class B & C fires.

Information Sources

- Compressed Gas Association
1725 Jefferson Davis Highway, Suite 1004
Arlington, VA 22202-4102
Phone: 1-703-412-0900
- National Fire Protection Association
1 Batterymarch Park, P.O. Box 9101
Quincy, MA 02269-9101
Phone: 1-800-344-3555

Emergency Response Telephone Numbers

USA

CHEMTRAC

1-800-424-9300 (Toll Free in the U.S., Canada, and U.S. Virgin Islands)
703-527-3887 for calls originating elsewhere (Collect calls are accepted)

CHEM-TEL, INC.

1-800-255-3924 (Toll Free in the U.S., Canada, and U.S. Virgin Islands)
813-248-0585 for calls originating elsewhere (Collect calls are accepted)

INFOTRAC

1-800-535-5053 (Toll Free in the U.S., Canada, and U.S. Virgin Islands)
352-323-3500 for calls originating elsewhere (Collect calls are accepted)

3E COMPANY

1-800-451-8346 (Toll Free in the U.S., Canada, and U.S. Virgin Islands)
760-602-8703 for calls originating elsewhere (Collect calls are accepted)

NATIONAL RESPONSE CENTER (NRC)

Call NRC (24 Hours)

1-800-424-8802 (Toll Free in the U.S., Canada, and U.S. Virgin Islands)
202-267-2675 in the District of Columbia

MILITARY SHIPMENTS

703-697-0218 Explosives/Ammunition Incidents (Collect calls accepted)
1-800-851-8061 All other dangerous goods incidents

NATIONWIDE POISON CONTROL CENTER (United States Only)

1-800-222-1222 (Toll Free in the U.S.)

CANADA

CANUTEC

613-996-6666 (Collect calls are accepted)
*666 Cellular (In Canada only)

Visit Web Site: www.cstusa.biz for further information

or

Call 410-982-6585

or

Ask your local sales representative