Handling liquefied compressed gas

A liquefied compressed gas can be defined as a gas, which when compressed in a container, becomes a liquid at ordinary temperatures and at pressures ranging from 25 to 2500 psig. Liquefied gases have boiling points that range from –130°F to 30°F (–90°C to –1°C). At 70°F (21.1°C) the cylinder contains both liquid and gas. Cylinder pressure, or the "vapor pressure" of the gas, is directly affected by ambient temperature. Increases or decreases in the temperature will cause the vapor pressure to increase or decrease, respectively.

Liquefied gases are packaged under their own vapor pressure and are shipped under rules that limit the maximum amount that can be put into a container to allow for liquid expansion with rising temperatures. (The various transportation regulatory agencies have established very detailed requirements for the filling limits of liquefied compressed gases to prevent the possibility of container overpressurization. Consult the regulations for your region for more information.)

Typical liquefied compressed gases are listed in **Table 1**.

Containers

Liquefied compressed gases come in a variety of containers.

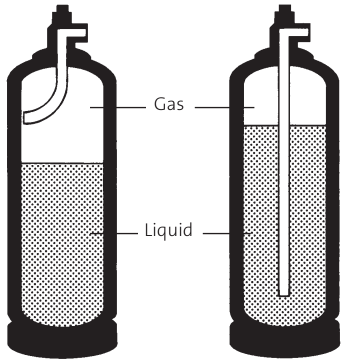
Because the product exists in both the liquid and gas phases in the container, many containers are equipped to access both phases. This is accomplished by the use of full-length eductor tubes (dip tubes) and gooseneck eductor tubes **(see Fig. 1)**.

Cylinders with a full-length eductor tube, or what is sometimes called a full-length dip tube, have a tube that runs from the inlet of the cylinder valve to the bottom of the cylinder. When a cylinder with this valve configuration is in the upright position, the inlet of the tube is immersed in liquid, and the liquid phase will be removed.

Some cylinders are equipped with two valves: one having a full-length eductor tube for liquid withdrawal and the other a valve without an eductor tube for gas withdrawal or inert gas padding (**see Fig. 2** and section on liquid-phase withdrawal).

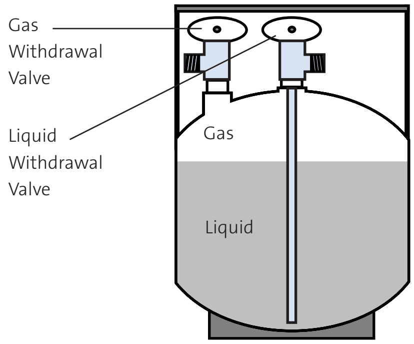
Another type of valve configuration is called the gooseneck eductor tube. The gooseneck goes only a short distance into the cylinder and then bends to the cylinder side opposite the valve outlet. In the upright position, the gooseneck is above the liquid level and provides gas. To remove the liquid, the cylinder is placed on its side with the valve outlet facing up. This puts the gooseneck into the liquid.

Figure 1:



(left) Cylinder with gooseneck dip tube. (right) Cylinder with full-length dip tube.

Figure 2:



Some cylinders are equipped with two valves, one with and one without an eductor tube.

In larger horizontal containers, such as high pressure "Y" cylinders, low pressure ton containers (multi unit tank car tank), and tube trailers **(see Figs. 3, 4, and 5)**, dip tubes are required to access both the liquid and gas phases.

"Y" cylinders use what is referred to as a "C" configuration. This configuration is very similar to the gooseneck, but the inlet to the gooseneck is oriented in the same direction as the valve outlet. The product flows into the dip tube and out the valve outlet in a flow path shaped like the letter "C." This means when the valve outlet is pointed up, the gas phase is accessed, and when the valve outlet is pointed down, the liquid phase is accessed.

Ton containers have two valves. The container is oriented so the valves are one above the other. The valves are connected to dip tubes that run to the cylinder sides. The top valve will have the dip tube in the vapor, and the bottom valve will have the dip tube in the liquid.

On tube trailers with liquefied compressed gases, gooseneck dip tubes are used, but the dip tube orientation is determined by the end of the tube trailer that is being accessed. Typically all valve outlets will be aimed downward on a tube trailer. Normally, gas can be withdrawn from the rear of the trailer with all dip tubes oriented upward (to the vapor phase). Liquid can be withdrawn from the front of the trailer where the dip tubes will be oriented downward into the liquid phase.

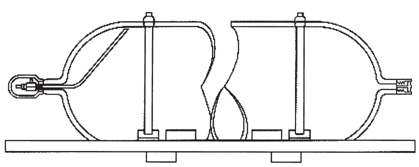
The most common type of liquefied gas container uses a standard cylinder valve. In the upright position the liquid level is well below the valve inlet, preventing liquid from being removed. If liquefied gas is to be withdrawn, the bottom of the cylinder must be elevated above the valve to allow the liquid phase to be in contact with the valve inlet. Special inversion racks are usually used to provide a safe method for cylinder inversion.

Table 1: Some Common Liquefied Gases*

Gas	Vapor Pressure @ 70°F (21.1°C)
Ammonia	114 psig (7.76 atm)
Carbon Dioxide	830 psig (56.5 atm)
Chlorine	86 psig (5.85 atm)
Hydrogen Chloride	613 psig (41.7 atm)
Hydrogen Sulfide	247 psig (16.8 atm)
Methyl Chloride	59 psig (4.01 atm)
Monomethylamine	44 psig (2.99 atm)
Nitrous Oxide	745 psig (50.7 atm)
Sulfur Dioxide	34 psig (2.31 atm)
Sulfur Hexafluoride	298 psig (20.3 atm)
Tungsten Hexafluoride	2.5 psig (0.17 atm)

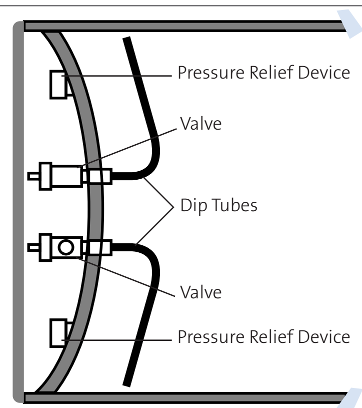
* Liquid petroleum gases, such as propane and butane, have not been included as they are too numerous to mention.

Figure 3



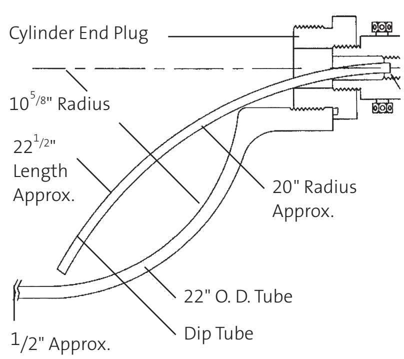
"Y" cylinders use a C configuration dip tube.

Figure 4



Ton containers have two valves, each connected to a dip tube.

Figure 5



Tube trailer front dip tube configuration.

How to withdraw product safely

Product withdrawal should be carefully supervised by qualified people with the proper equipment. Personnel should be aware of the associated hazards of the product and equipment and thoroughly understand applicable safety regulations and emergency procedures.

There are two different methods of product withdrawal from a liquefied compressed gas container: as a vapor (gas) or as a liquid (liquefied gas).

Vapor-phase withdrawal

Liquefied compressed gases in a cylinder or any container exist in liquid and gaseous form at a pressure equal to the vapor pressure of the particular gas (see **Table 1** for specific vapor pressures). The cylinder pressure will remain constant at the vapor pressure of the material as long as there is any liquid remaining in the cylinder. When the contents of the cylinder are withdrawn to the point that no liquid remains, the pressure in the cylinder will begin to diminish as the remaining vapor is used.

The first step for removing vapor is to orient the package to access the vapor phase of the product.

When vapor is removed from the cylinder, the temperature and pressure equilibrium is disturbed, and both will decrease. Liquid will vaporize to replace the gas that was removed, absorbing the heat of vaporization from the remaining liquid and the container. This heat can usually be recovered from the ambient air surrounding the cylinder. If the withdrawal rate of the gas is such that the energy required to vaporize the liquid cannot be recovered from the surrounding air, the liquid phase will begin to cool.

The phase equilibrium is a function of the system temperature. As the temperature of the liquid phase increases, so will the vapor pressure; the converse is also true. If the liquid cannot recover enough heat from its surroundings to keep up with the demand for gas, the liquid will cool. This is called "sub-cooling" or "auto-refrigeration." It is common for vapor withdrawal to cool the cylinder to the point where moisture condenses on the external cylinder, valve, and piping surfaces. If the surfaces are chilled below water's freezing point, the condensed moisture can solidify into ice.

If the rate of withdrawal of vapor is excessive, serious safety problems can arise. Sub-cooling can cause the vapor pressure to collapse to the point where the cylinder pressure is below that of the process. This pressure inversion can cause backflow of the process materials into the cylinder, or "suckback." It is also possible to cool a cylinder enough to actually embrittle the metal, potentially leading to a cylinder failure. Ice formation on the cylinder and especially on the valve and piping, coupled with the decrease in flow as the cylinder pressure drops, is sometimes misinterpreted as blockage in the valve. This can lead to users applying excessive heat to the valve, possibly creating leakage at the outlet

Special warnings regarding vapor-phase withdrawal

CAUTION! EXCESSIVE TEMPERATURE CONSIDERATIONS: Any enhanced vapor withdrawal method listed here that involves heating should be controlled to prevent exposure of the container to temperatures exceeding 125°F (52°C).

DANGER: Never heat an aluminum cylinder with electrical resistance elements. Only cylinders made of steel should be electrically heated. Aluminum cylinders can be severely damaged by excessive temperature exposure.

CAUTION! ELECTRICAL REQUIREMENTS: All electrical systems for indirect heating and monitoring for a flammable gas supply system should be designed to comply with the applicable national or local electrical code requirements. Typical electrical code requirements include classification for instruments and/or limiting the surface temperature of heated resistance elements to a specified fraction of the autoignition temperature for the flammable gas.

AIR PRODUCTS' POSITION ON CODES: Various national and/or local codes prohibit the general direct heating of containers. However, these codes are interpreted as only pertaining to heating systems that apply heat energy directly onto the containers.

This interpretation is based on the examples of prohibited heating methods cited in various code references: radiant flame, steam impingement on the container, immersion in a heated water bath or electrical resistance heater elements in direct contact with the container.

Nonheated, flow-enhancing options should be evaluated as a first preference. If none are suitable, a properly engineered and approved **INDIRECT** heating system is acceptable for liquefied compressed gas containers. Direct heating methods such as flames, steam impingement, electrical resistance elements, water bath immersion, hot plates, and ovens should not be used.

Water-bath immersion is not recommended: The direct immersion of a cylinder into a water bath is **NOT RECOMMENDED** as a heating method, since repeated or prolonged exposure to heated and agitated water can degrade the cylinder's external surface and can eventually compromise the cylinder's mechanical integrity. Use of acidic or alkaline water or the use of conditioning salts and other materials has caused cylinder failures when used in water baths.

connection, the valve packing, and especially from a fusible metal relief device if the valve is so equipped.

How can one improve the gas-phase withdrawal rate?

Depending on the cylinder or container geometry and ambient conditions, some method might be necessary to enhance product withdrawal from liquefied compressed gas cylinders to maintain required flow rates. This is especially true with small cylinders and nearly empty larger containers.

Product withdrawal enhancement methods have a definite preference of selection based on inherent safety considerations and consequences of system failure. This Safetygram presents the recommended methods in order of preference and their associated requirements.

1. **Use a Larger Container:** This will increase the outer surface area of the container to allow more heat transfer from the environment.
2. **Vaporization:** The user can withdraw liquid phase through an external vaporizer, thereby converting the liquid to gaseous product. This is the preferred method for high flow requirements. This method requires liquid-phase withdrawal from the container using an eductor tube. The liquid is then vaporized via a standard vaporizer, tubing coil, or other vaporization means. This method can provide the highest withdrawal rates, but may not be suitable for high-purity applications. It also creates the highest release flow rate potential due to downstream leakage or operator error, which should be adequately addressed for hazardous products. Overpressure protection should be provided on any lines, including the vaporizer circuit, in which liquid product can be trapped by isolation valves, check valves, or other system components.
3. **Container Switching:** This method uses two or more identical containers or banks of containers that can be switched to the online position either manually or automatically. When the primary, active container vapor pressure drops below the threshold capable of supplying the desired gaseous flow rates, the secondary, alternate container is brought online in place of the previously active container. This permits the first container to rewarm by absorbing ambient heat. The switching sequence is repeated throughout the high flow demand. This method may not be feasible if the ambient temperature conditions do not provide adequate heat to rewarm the off-line container within an acceptable period of time.
4. **Container Manifolding:** Manifolding a number of liquefied, compressed gas containers in parallel permits the user to achieve the required gaseous flow rate by withdrawing product from all containers simultaneously. This method benefits from the larger thermal mass of the manifolded cylinders and product and provides additional container surface area for ambient heat transfer, thus enhancing total gaseous withdrawal capability. However, manifolding may not be adequate if ambient temperature conditions do not yield sufficient heat flow or product vapor pressures within the containers.

Warning: Manifolding liquefied compressed gas cylinders, together without good engineering practices to prevent product migration of one cylinder's contents into another cylinder, may result in:

1. Container rupture.
2. Major property damage.
3. Serious injury or death.
4. Noncompliance with local, national or international shipping and fire/occupancy regulations.

CAUTION, Cylinder Heating Considerations: Any equipment used to heat a cylinder of liquefied compressed gas must include redundant over-temperature protection, such as a system temperature controller (thermostat) with a maximum setpoint of 125°F (52°C) along with a separate, independent over-temperature shutdown device, such as a fusible link, in the power supply to the heater. The over-temperature shutdown must be installed between the heat source and the cylinder.

5. **Convective Conditioning:** Gas withdrawal can be enhanced by heating the atmosphere surrounding the container to provide additional thermal convective heating of the containers and their contents to increase product vapor pressure. This approach is best accomplished if the container is held within an enclosure or small room and it provides gradual, controlled heating of the container contents. However, this system may not prove feasible for containers located outdoors, within a large room, or in a highly ventilated/exhausted enclosure.

6. **Radiant Conditioning:** Heat lamps (or equal) can be used to provide radiant heating of the container contents to increase container pressure for enhanced gas withdrawal capability. The heat source must not directly heat the container valve since the valve, connection, and relief device components can be damaged by excessive temperatures. This method is best utilized for indoor systems with no obstructions around the containers and provides gradual heating of the container contents. The system may not be feasible for containers located outdoors or in congested areas.

7. **Temperature-Controlled Jacket:** This method encloses the container in a removable, temperature-controlled jacket that contains a "closed-loop," recirculated heat transfer fluid connected to a separate electric heater unit. This design separates the heating element from the container and also allows for heating or cooling the containers, depending on the process pressure requirements. The electric heater should have a heat output rated for the maximum product withdrawal rate requirements, without excessive overcapacity. This design is widely used for multiple container systems where there is sufficient space to locate the heating unit adjacent to the containers.

8. **Electrically Heated Blanket:** The container can be encased in a removable blanket that contains electrically heated resistance elements operated by a temperature controller. Blankets should have an integral covering permanently attached to their inner surface to prevent direct contact of the heating elements with the container. The power input to the blanket should be limited, based on maximum withdrawal rate requirements to restrict worst-case heat input to the container during temperature controller runaway.

Liquid-phase withdrawal

Just as in vapor-phase removal, the first step in liquid-phase removal is to orient the package to gain access to the liquid phase. The liquid is pushed from the cylinder by the vapor pressure of the product. As the liquid is removed, it increases the volume of the vapor space of the cylinder. Some liquid will vaporize to fill the additional space, but usually not enough to excessively sub-cool the cylinder.

Sometimes the vapor pressure of the product is not high enough to push the liquid out at the required rate. When this is the case, a method called padding can be used to pressurize the liquid. This enhances the rate at which the liquid can be pushed from the cylinder. Padding is the addition of an inert gas to the vapor space in the cylinder to raise the cylinder pressure. When adding the inert gas to the cylinder, the cylinder pressure rating must never be exceeded. This pressure rating is part of the regulatory stamping on the cylinder. The maximum allowable working pressure (MAWP) of the cylinder is stamped into the cylinder. In the United States the stamping may read DOT3AA480, where 480 psig is the MAWP. In Europe the stamping may read FP25BAR, where 25 BAR is the MAWP. Furthermore, certain cylinder relief devices may vent the cylinder contents at pressures below the pressure rating of the cylinder. If you are not sure how to interpret the DOT stamping, or for guidance concerning padding a cylinder, contact your supplier.

How the inert gas pressure is added depends upon the cylinder. If the cylinder has dual valves, the inert gas can be added through the gas-phase valve. Be sure the inert gas source is regulated to not exceed the pressure rating of the cylinder and is protected from backflow minimally by a check valve. If the cylinder has one valve, the inert gas can be added while the cylinder valve is oriented to the vapor phase, then the inert gas source can be disconnected before orienting to the liquid phase. Again, care must be taken not to exceed the pressure rating of the cylinder. Some applications use air in place of the inert gas for padding. For some products, unloading with air padding may be prohibited by regulations. **NEVER USE AIR TO PAD FLAMMABLE PRODUCTS.** When air padding is allowed and appropriate, it is imperative that clean, oil-free, cooled, dry compressed air be introduced into the vapor space through its vapor valve to transfer the liquid. **NEVER** use a plant air system for air padding since vapors may backflow into the plant air system.

Extreme care must be taken when handling the liquid phase of any liquefied compressed gas. Unlike gas, the liquid does not compress. Therefore, the liquid must always have a space to expand, especially as it warms. In the cylinder, this expansion space is provided by the vapor space or head space.

The filling limits/fill density for liquefied compressed gases were described earlier. These limits were set to prevent the cylinder from becoming liquid full at normal storage and use temperatures. If a vessel or system becomes liquid full, any increase in temperature would cause the liquid to try to expand with no space for the expansion. The liquid's incompressibility would result in a rapid increase of hydrostatic pressure. These pressures can build very rapidly and can quickly cause overpressurization of the equipment. Overpressurization of a system takes place when its pressure rating is exceeded. This can result in a rupture of the system. Systems using liquefied gases as liquids should be adequately protected by pressure relief devices, especially where there is a chance to trap liquid between valves or in other components that can be isolated.

Important considerations

1. **NEVER** allow any part of a liquefied gas container to be exposed to temperatures greater than 125°F (51°C).

2. **NEVER** fill any cylinders without the owner's written consent.

3. **NEVER** heat an aluminum cylinder with electrical resistance heaters.

4. **ALWAYS** refer to the Material Safety Data Sheet for specific chemical properties.

Manufacturers of systems to enhance withdrawal rates

Consult the *Thomas Register* to locate vendors of cylinder heating systems or vaporizers. Or contact the Air Products Gases and Equipment Technical Information Center at +1-800-752-1597.

Emergency Response System

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For regional ER telephone numbers, please refer to the local SDS 24 hours a day, 7 days a week for assistance involving Air Products and Chemicals, Inc. products

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