EHS Laboratory Guidance

Cryogenic Liquids[1]

Introduction

Cryogenic liquid is defined by the Idaho Fire Code as having a boiling point of less than -90º C (-130º F) at 14.7 psia (1 bar). All cryogenic liquids are gases at normal temperatures and pressures. When cooled and placed under pressure in specially designed systems or storage containers, the gases condense to a liquid state and maintain very cold temperatures. The most commonly used industrial gases that are transported, handled, and stored in the liquid state at cryogenic temperatures are argon, helium, hydrogen, nitrogen, and oxygen. General precautions and safe practices must be followed because of the extremely low temperatures and high rates of conversion into gas of all the cryogenic liquids. Specific precautions must be followed where a particular liquid may react with contaminants or may present other hazards associated with that particular product such as asphyxiation or flammability.

As always, end users should obtain and be thoroughly familiar with the Safety Data Sheet (SDS) for their specific product. All operators must be familiar with the instructions for equipment to be used with the cryogenic liquid.

General Safety Precautions

Many of the safety precautions observed for gases in the gaseous state also apply to the same gases in the liquid state. However, each cryogenic liquid has its own unique properties. Be familiar with the unique properties of the product being used.

All cryogenic liquids have potential hazards that stem from the following properties:

1. Cryogenic liquids are extremely cold. Cryogenic liquids and their vapors can rapidly freeze human tissue and can cause many common materials such as carbon steel, rubber, and plastic to become brittle or even break under stress. Cryogenic liquids in containers and piping at temperatures at or below the boiling point of liquefied air [-318°F (-194°C, 79°K)] can condense the surrounding air and cause a localized oxygen-enriched atmosphere. Extremely cold cryogens such as hydrogen and helium can even freeze or solidify the surrounding air.
2. Cryogenic liquids produce large volumes of gas when they vaporize. For example, one volume of liquid nitrogen at atmospheric pressure vaporizes to around 694 equivalent volumes of nitrogen gas at 68°F (20°C). A cryogenic liquid cannot be indefinitely maintained as a liquid even in well-insulated containers. If these liquids are vaporized in a sealed container, they can produce enormous pressures that could rupture the container. For this reason, pressurized cryogenic containers are normally protected with multiple devices for over-pressure prevention. Common pressure-relief devices include a pressure-relief valve for primary protection and a rupture disc for secondary protection. All sections of equipment that may allow for the liquid to become trapped must be protected by a

pressure-relief device, as shown in Figure 1. The product vented by these relief devices should be routed to a safe outdoor location or a well-ventilated area.

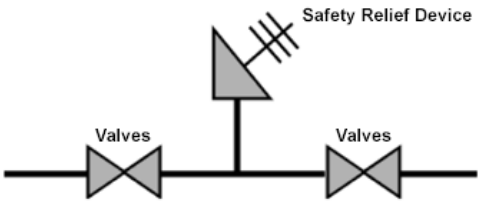

Fig. 1 Potential for trapping liquid between valves.

3. Vaporization of a cryogenic liquid, except oxygen, in an enclosed area can cause asphyxiation by the displacement of air. Vaporization of liquid oxygen in an enclosed area can cause oxygen enrichment, which could saturate combustibles in the area such as workers' clothing. This can cause a fire if an ignition source is present. Although oxygen itself is not flammable, it will support and vigorously accelerate the combustion of other materials.

Most cryogenic liquids and their gases are odorless, colorless, and tasteless, except liquid oxygen, which is light blue, thus making it difficult to detect when a leak occurs. However, extremely cold liquids and their vapors have a built-in warning property that appears whenever they are exposed to the atmosphere: the cold, boiled-off gases condense the moisture in the surrounding air, creating a highly visible fog. This fog can form around cold equipment even when no release of the cold liquid or vapors has occurred. However, the vapor cloud extends beyond the visible fog cloud. The fog cloud is simply the area where the vapors are cold enough to condense the moisture in the air. The vapors can extend well beyond the fog cloud depending on the product and atmospheric conditions. Although fog clouds may be indicative of a release, they must never be used to define the leak area and thus should not be entered by anyone. The dense fog clouds associated with the handling or transfer of cryogenic liquids can obstruct visibility. Care should be exercised so that any fog or vapor clouds do not interfere with vehicle traffic or safety escape routes.

Cryogen Containers

Cryogenic liquids are typically shipped in low-pressure, vacuum-insulated, multi-walled containers, and may be transferred to non-pressurized containers for everyday use. The vacuum-insulated wall design is intended to keep the surrounding heat away from the liquid contained in the vessel. The types of containers commonly used at the University of Idaho are the dewar and the cryogenic liquid cylinder.

- **Liquid dewar flasks**: Figure 2 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.

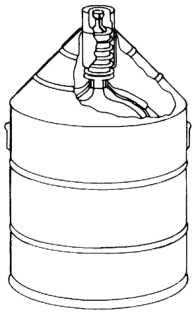
Fig. 2 Typical dewar

- **Liquid cylinders**: Figure 3 shows a typical cryogenic liquid cylinder. Cryogenic liquid cylinders are insulated, vacuum-jacketed pressure vessels. They come equipped with safety relief valves and rupture discs to protect the cylinders from pressure build-up. These containers operate at pressures up to 350 psig and have capacities

between 80 and 450 liters of liquid. Product may be dispensed as a gas by passing liquid through an internal vaporizer or as a liquid under its own vapor pressure.

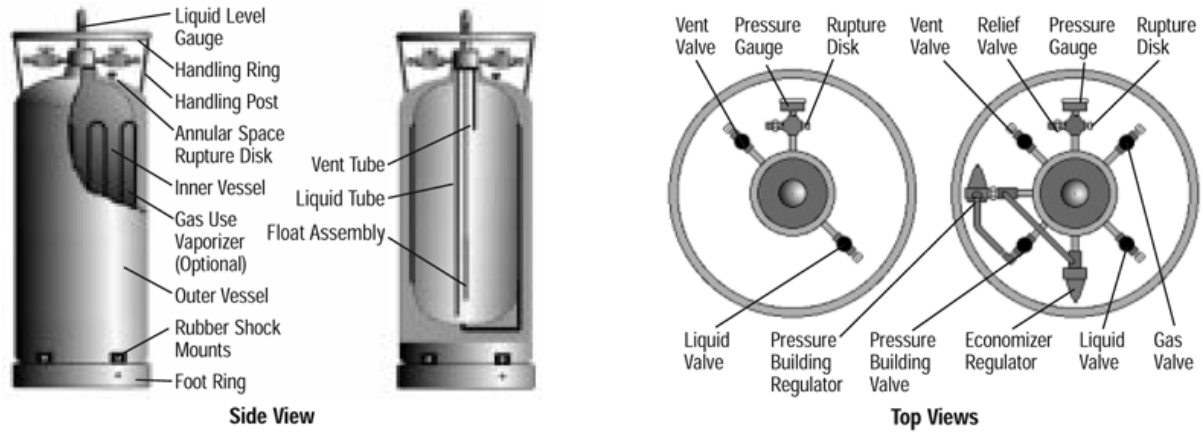

Fig. 3: Typical cryogenic liquid cylinder, side and top views

Safe Work Practices

- Avoid contact of the skin with cryogens or items that have been super-cooled by a cryogen, as these can cause severe burns or frostbite. The vapors coming from these liquids are also extremely cold and can produce burns. Remove jewelry or other items that could trap spilled liquids against the skin.
- Wear eye protection and a face shield when opening valves, dispensing cryogenic liquids, or placing items into or removing items from a cryogen. If eye or skin contact occurs, immediately remove restrictive clothing, flush the affected area with tepid water and seek medical attention. Do not rub the affected area or use dry heat to warm.
- Use thermal or leather gloves when touching items that have been in contact with cryogens. Use tongs to remove or place items into cryogenic liquids. Use potholders when opening valves or dispensing cryogens. Splattering will occur anytime an item is placed into or removed from a cryogenic liquid.
- Items removed from a cryogen will change temperatures/pressures very rapidly, which can result in container failure sending shards of plastic everywhere. Allow vials and other containers that have been in contact with cryogens to warm slowly to minimize sudden pressure differentials.
- Cryogenic gases can cause asphyxiation by displacing oxygen in the air because of their very large expansion ratios. Indoor use, including storage and dispensing areas, should be mechanically ventilated (minimum of six air changes per hour).
- Pre-plan for spills. Know the maximum amount that can be spilled or released in the area without creating an oxygen deficient atmosphere or other hazard (e.g., fire, toxic atmosphere, etc.). If a spill occurs that exceeds this amount, immediately leave the area and shut doors. If the amount spilled or released is such that it could impact nearby areas or create a secondary hazard of fire or toxicity, initiate building evacuation procedures by activating the nearest fire alarm pull station.
- Do not block, seal, or otherwise tamper with the pressure relief valves. Caps on dewars are designed to be loose-fitting to allow gases to escape. Never completely seal a dewar.

- When working with cryogenic liquids, ensure that equipment is scrupulously clean. Greases, waxes, or other impurities could react with the liquid/gas or condensed room oxygen to cause a fire. Use and store cryogens away from ignition sources.
- Store and move cylinders only in an upright position. Do not drop, tip, or roll containers. Use mechanical handling devices for safely moving large containers and secure the container during transport (Figure 4).
- Use only cryogenic storage vials that are designed specifically for this purpose, and visually inspect each vial prior to use to ensure that there are no defects.

Fig. 4: Cylinder cart

Personal Protective Equipment (PPE)

One must be thoroughly familiar with the properties and safety considerations before handling a cryogenic liquid and its associated equipment. The eyes are the most sensitive body part to the extreme cold of the liquid and vapors of cryogenic liquids. The minimum recommended personal protective equipment for handling cryogens includes (Figure 5):

- a face shield over safety glasses,
- loose-fitting thermal insulated or leather gloves,
- long sleeve shirt or lab coat, and
- long pants or trousers without cuffs.

A cryogen apron and safety shoes are highly recommended for people involved in the handling of larger cylinders. Depending on the application, special clothing suitable for that application may be advisable.

Fig. 5: PPE

A special note on insulated gloves: Gloves should be loose-fitting such that they are able to be quickly removed if cryogenic liquid is spilled on them. Insulated gloves are not made to permit the hands to be put into a cryogenic liquid. They will only provide short-term protection from accidental contact with the liquid.

In emergency situations, self-contained breathing apparatus (SCBA) may be required for first responders.

Special Inert Gas Precautions

The potential for asphyxiation must be recognized when handling inert cryogenic liquids. Because of the high expansion ratios of cryogenic liquids, air can quickly be displaced. Oxygen monitors are recommended whenever cryogenic liquids are handled in enclosed areas. People should not be permitted in atmospheres containing less than 19.5% oxygen without supplied air. Liquid helium has the potential to solidify air, which can block pressure-relief devices and other container openings. This can result in pressure buildup that may rupture the container.

Special Oxygen Precautions

Do not allow open flames in any areas where liquid oxygen is stored or handled. Do not permit liquid oxygen or oxygen-enriched air to come into 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 spill area. Keep sources of ignition away for 30 minutes after all frost or fog has disappeared. Any clothing that has been splashed or soaked with liquid oxygen or exposed to high oxygen concentrations should preferably 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.

Special Hydrogen Precautions

Do not permit smoking, open flames or other sources of ignition in any area where liquid hydrogen is stored or handled. All major pieces of equipment should be properly grounded. All electrical equipment and wiring should be in accordance with national fire and electrical standards, including but not limited to (1) Idaho Fire Code Chapters 55 and 58 and (2) Idaho Division of Building Safety General Health & Safety Standard 210. Boiled-off gas from closed liquid hydrogen containers used or stored inside buildings must be vented to a safe location. Liquid hydrogen should not be poured from one container to another or transferred in an atmosphere of air. If this is done, the oxygen in the air will condense in the liquid hydrogen, presenting a possible explosion hazard. Liquid hydrogen also has the potential of solidifying air which can block safety relief devices and other openings, which may lead to rupture of the container. Dewars and other containers made of glass are not recommended for liquid hydrogen service. Breakage makes the possibility of explosion too hazardous to risk. Every effort must be made to avoid spills, regardless of the rate of ventilation, because it is impossible to avoid creating a flammable vapor cloud.

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 build-up or an external pressure source to remove the liquid. For cryogenic liquid cylinders, the transfer line is connected to the cylinder liquid withdrawal valve. Liquid product is typically removed through insulated withdrawal lines to minimize the vaporization 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. Liquid cylinders designed to dispense gases 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 they are different than the connections used for gaseous withdrawal. This is to prevent accidental introduction of liquid into a gas system, or of gas into a liquid system.

First Aid

People suffering from lack of oxygen should be moved to fresh air. If the victim is not breathing, contact 911 and begin CPR. Self-contained breathing apparatus (SCBA) may be required to prevent asphyxiation of rescue personnel.

For skin contact with a cryogenic liquid, 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 that has a temperature not in excess of 105°F (40°C). Never use dry heat. Contact 911 as soon as possible.

Fig. 6: Liquid nitrogen burn

Frozen tissue is painless and appears waxy with a possible yellow color. It will become swollen, painful, and prone to infection when thawed (Figure 6). 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 the case of massive exposure, contact 911, then remove clothing while showering the victim with warm water.

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

[1]Adapted from information taken from the Air Products' website with permission.