

Working with Cryogenic Liquids

Cryogenic liquids are liquefied gases that must be maintained at very low temperatures to remain a liquid. Cryogenic liquids by definition are very cold, typically having a boiling points below -150°C (-238°F). At room temperature these liquids boil off and become gas. They are odorless and colorless therefore able to escape their containers unnoticed by those in their presence. Cryogenic liquids have many uses in the lab including technical applications such as in neutrino experiments, cooling of NMR and MRI magnets, or preserving tissues and other samples for research. Although liquid nitrogen, argon and helium are the more common cryogens it is important to be aware of other liquid cryogens such as oxygen, methane and hydrogen.

Anyone who will work with or around cryogens should be trained, and made aware of the hazards involved. The training should provide information on the following topics:

- Hazards of the cryogen
- Personal Protective Equipment (PPE) requirements
- Specific instructions on the equipment being used
- Standard Operating Procedures
- Exposure and Emergency Response

Hazards

The primary hazards associated with cryogenic liquids are their extreme cold temperatures, which can lead to cold burns or frostbite, and oxygen deficient environments. Additionally, there is the potential for pressurization of containers, embrittlement of materials. Some cryogenics are also flammable or can greatly increase the flammability of other materials.

| Cryogen | Boiling point ($^{\circ}\text{F}$) | Critical pressure | Liquid density, g/L | Gas density (27°C), g/L | expansion ratio | Type of gas |
|-----------------|--------------------------------------|-------------------|---------------------|---|-----------------|-------------|
| Ar | -303 | 710 | 1402 | 1.63 | 860 | Inert |
| He | -452 | 34 | 125 | 0.16 | 780 | Inert |
| H ₂ | -423 | 188 | 71 | 0.082 | 865 | Flammable |
| N ₂ | -321 | 492 | 808 | 2.25 | 710 | Inert |
| O ₂ | -297 | 736 | 1410 | 1.4 | 875 | Oxygen |
| CH ₄ | -256 | 673 | 425 | 0.72 | 650 | Flammable |

Cold Temperature

As seen in the table above, the most obvious hazard with cryogenic liquids are the extreme cold temperatures associated with them. When filling tanks or dewars with cryogenics you'll want to cover your legs, feet, arms, hands and face to protect against splashes. The basic PPE that should be worn when working with any of the above mentioned chemicals includes goggles, long sleeved shirts, long pants, and closed-toed shoes. The shoes should cover your whole foot and be thick enough to actually protect your foot from the cryogen. Running shoes and ballet flats for example wouldn't provide much protection in this situation. If you are wearing thermal gloves they should be loose-fitting so they are able to be quickly removed if cryogenic liquid is spilled on them. Keep in mind that gloves only provide short-term protection from contact with the liquid.

Additional PPE will be dictated by the type of cryogen being used and the procedure being performed (see below).

When preparing to fill dewars or tanks face shields and thermal gloves are recommended. Keep in mind that these containers are probably warm in comparison to the temperature of the cryogen. You should start filling them very slowly so that the vessel has time to cool to the appropriate temperature. When you start filling them it is not uncommon to get some splashing.

Lastly, remember that the cold temperatures are not only for the liquids themselves but also for anything that the cryogenics have been in contact with – especially metals. Be careful when touching any surface that has been in contact with cryogenic liquids.

In case of skin exposure to cryogenics such as liquid nitrogen, argon or helium, rinse the area in warm water. Don't rub the affected area because the skin may be fragile and susceptible to tearing. If your clothing is exposed it may be necessary to remove it before it has a chance to react with your skin.

Oxygen Deficiency

We have previously covered the concept of oxygen deficiency with regards to liquid nitrogen (see "[Liquid Nitrogen - The Unseen Danger](#)"). The same concept holds true for all cryogenic liquids. The table above shows the expansion ratio for the common cryogenic liquids. A spill or release of a cryogen has the potential to quickly generate a harmful, if not lethal, environment. When working with cryogenic liquids it's important to implement the proper safety protocols. If there is a possibility of oxygen levels falling below the safe breathing range (19% - 20.9% oxygen) signage must be in place to notify workers and the public of the hazards in that space. In some instances it may be necessary to have monitors that will sound if the oxygen levels drop to harmful levels. Anyone working with cryogenic liquids should be trained not only on handling procedures but specific warning systems for identifying oxygen deficient areas and the procedures for dealing with these emergencies.

There are a couple common unsafe practices that everyone should avoid:

When storing cryogen containers indoors they should be kept in a well-ventilated room. The containers storing most inert cryogenic liquids are built to insulate and keep the cryogen for reasonable period of time. Some dewars are designed to build up pressure to allow transfer of the liquid. These are also designed to vent to release pressure that eventually builds up. Never store these in cold rooms. While it may seem like storing these tanks in a cold room will help keep the cryogen longer, this is not the case. Even at a colder temperature the tanks will slowly vent. Storing Cryogenic tanks in unventilated cold storage areas can pose a serious risk to an unsuspecting person walking into the unforeseen danger of an oxygen-depleted atmosphere.

When moving cryogenic liquid containers, make a plan before you start. Do not move a container by rolling it on its side. Always use a hand truck or cart and a strap or chain to secure the container to the handcart making sure to keep the containers upright. If cryogenics must be transported by elevator, plan to have someone awaiting the tanks arrival on the desired floor. Send cryogenics in elevators alone. If a person is on an elevator that loses power or gets stuck they would be trapped in a confined space with the cryogen and a potentially oxygen deficient atmosphere. For this reason public elevators should not be used for this task. Freight elevators are the best choice because they go directly to the selected floor uninterrupted.

Never leave a tank alone while its being filled. This could lead to overfilling the tank and spillage, putting yourself and others at risk. In a scenario like this you'd be forced to either walk through a cryogen spill to turn off the tank or be forced to evacuate the premises.

Rooms where significant amounts of cryogenic liquids are stored, used, or transferred should be evaluated by EH&S for proper engineering controls and alarms.

Flammability of Cryogenic Liquids

Besides the more common inert cryogenics, there are some cryogenic liquids, such as hydrogen and methane that are flammable. Liquid hydrogen is a rocket fuel and is also used to cool neutrons for neutron scattering. It is easily ignited and is a serious fire hazard. It has a wide flammability range and can burn at as little as 4% of air volume. The flame produced by it is colorless and difficult to see. Additionally, since liquid hydrogen is colder than the boiling point of liquid oxygen there is a potential for liquefying oxygen leading to a significant explosion hazard. Extreme precautions need to be taken when working with this chemical. It is prudent to limit the amount of liquid hydrogen used indoors. If a fire starts you must first turn off the gas flow, if it can be done without putting yourself at risk.. If the hydrogen supply cannot be turned off it may be best to allow it to burn while keeping the fire contained. Attempting to smother the fire while gas is still flowing could cause re-ignition or an explosion.

Methane is another gas that is sometimes used in cryogenic form. Similar to hydrogen, it poses a flammability risk. However, it does not condense oxygen.

Liquid oxygen poses fire risks in that it can cause items that are non-combustible to burn readily. Organic substances react violently with it. If a fire starts in an area where liquid oxygen is flowing it's important to stop the flow by shutting off the valve. Remove clothing that is splashed with liquid oxygen immediately and air it out as it can remain flammable for hours.

WHENEVER handling a flammable cryogen or liquid oxygen PPE should include a flammable resistant lab coat along with less flammable clothing under the lab coat, such as clothing made of cotton or wool.

Pressurization of Containers

When treating samples with liquid nitrogen the container should never be completely closed unless the container is specifically designed for liquid nitrogen. As the container warms, pressure will build causing the container to crack or explode.

Embrittlement of materials

One last hazard that should be considered is the effects that the cold temperatures have on the structural integrity of materials. Many have seen demonstrations of common objects such as bananas or pieces of rubber being placed in liquid nitrogen and then being shattered. Consider carefully the design of any system which uses cryogenic liquids to ensure that all materials are compatible. Latex hoses for example, should be used instead of tygon because it can withstand the extreme cold of liquid nitrogen.

Liquid oxygen is not frequently used on campus, but there have been instances where oxygen has been accidentally condensed in liquid nitrogen cooled traps used to capture solvents and other contaminants in vacuum systems – a common example being the traps used with Schlenk lines in chemical syntheses. Nitrogen has a lower boiling point than oxygen so any leaks in the system can lead to oxygen in the atmosphere being collected along with other organic materials. As mentioned above, liquid oxygen can form an explosive mixture with organic substances. If you see a pale blue color in a trap, indicative of liquid oxygen, remove the liquid nitrogen dewar, vent the trap, close the sash of the hood, warn others of the danger, and leave the lab. Allow the trap to slowly warm and cautiously check every 30 minutes to see if the liquid oxygen has evaporated.

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