UNIVERSITY OF TEXAS ARLINGTON | ENVIRONMENTAL HEALTH & SAFETY

SAFE OPERATING PROCEDURE
CRYOGENIC FLUIDS

Definition
A cryogenic fluid or cryogen has a boiling point of less than -130°F/-89.9°C at 14.7 psia or an absolute pressure of 101.3 kPa. A cryogen is a liquefied or solidified gas.

Physical Properties

Cryogen	Temperature at 1 atm (°F /°C/ K)	Liquid-Gas Expansion Ratio	Pressure generated from trapped liquid allowed to warm to room temperature
Liquid O_2 (LOX)	-297 / -183 / 90.2	860 to 1	Not Specified
Liquid Ar (LAr)	-302 / -186 / 87.3	847 to 1	Not Specified
Liquid N_2 (LN2)	-320 / -196 / 77.4	696 to 1	43,000 psig
Liquid H_2 (LH2)	-423 / -253 / 20.3	851 to 1	25,000 psig
Liquid He (LHe)	-452 / -269 / 4.2	757 to 1	18,000 psig

Hazards
You must observe a number of general and specific safety practices when working with cryogens. Extremely low temperatures and high gas expansion ratios are generally applicable to all cryogens. However, specific cryogens have issues of reactivity, toxicity, and flammability.

THERMAL (low temperature). Contact with a cryogenic liquid, its off-gases, or components cooled to these low temperatures can readily cause frostbite or cryogenic burns. In addition, the accidental release of these cryogens into the work area can damage equipment and property (e.g., frozen water pipes, damaged flooring, damaged electrical cables and their insulation).

PRESSURIZATION. Cryogenic fluids, confined and allowed to warm, can generate very high pressures. LN2 confined and allowed to warm up to room temperature will generate a pressure of » 43,000 psig. The pressure similarly generated by LHe is 18,000 psig. Other cryogens behave in similar fashion. Dry Ice can generate hundreds of psig pressure if confined. This points out the potential for rupture of piping or vessels if appropriate venting and pressure relief is not provided. The function of vent lines can be defeated by the formation of ice (from condensed moisture) in the vent line. With LHe, air or other gases can be solidified to form this blockage. If a cryogenic fluid is subjected to a large amount of heat input, a flash vaporization can occur. This will result in a rapid pressure rise that can be described as a BLEVE (boiling liquid expanding vapor explosion). Vents and pressure relief devices should be vented to a safe location, considering the specific cryogen in question, the volume and flow rates of the potential releases, and the potential hazards presented by accumulation of the gases or liquids being vented.

OXYGEN DEFICIENCY/ASPHYXIATION. Cryogenic fluids have large liquid to gas expansion ratios, with LN2 » 680 to 1, (based on volume), LHe is » 740 to 1, and LAr » 820. With this in mind, note that any accidental release or overflow of these cryogenic liquids will quickly boil into the gas phase and may create an asphyxiation hazard by displacing the oxygen content of the surrounding area. In the case of LN2, the N_2 gas generated from malfunctioning equipment or spills of LN2 will be cold and denser than ambient air. Even well-ventilated lab spaces that have pits or other low-lying (or recessed) areas could have the oxygen displaced by this cold, dense N_2 gas. LN2 should not be used below the first floor of a building for this reason. Argon or CO_2 will also present these heavier-than-air hazards. Large-volume sources used in small laboratory spaces or in poorly ventilated areas increase the asphyxiation hazard. Oxygen monitors are strongly recommended for areas using inert cryogens; the minimum safe O_2 concentration in air is 19.5%.

ICE BUILD-UP. The temperatures associated with cryogenic liquids can easily condense moisture from the air and cause the formation of ice. This ice can cause a malfunction from the design intent of components or systems (e.g., plug vent lines and impede valve operation) or can damage piping systems. In the case of LHe and LH2, air itself can freeze solid and block vent lines. Building exhaust systems accidentally cooled to LN2 temperatures can also be damaged by ice formation or the weight of the accumulated ice and the weight of the LN2 itself. The resultant run-off water when the ice melts can also present a hazard.

MATERIALS CONCERNS. The low temperature of cryogenic liquids will adversely affect the properties of some materials resulting in system or vessel failure. The selection of the materials of construction for vessels and piping systems for cryogen handling should consider the appropriate behavior of the material at the cryogenic temperatures. In general, carbon steels and other bcc-structured metals can become brittle and fracture easily at cryogenic temperatures. Commonly-accepted materials of construction include fcc-structured metals such as the 300 series stainless steels, some of the aluminum alloys, and copper or brass. Plastics, such as Tygon® tubing, become brittle and can easily fail in cryogenic applications. Be sure to consult the appropriate references when selecting materials for cryogenic applications. Even when the appropriate materials are selected, thermal stresses that can lead to failure can be generated in some applications. Thermal gradients across a material or piping system or the rapid cool-down of a vessel can generate thermal stresses. The joining of materials with dissimilar coefficients of expansion can also generate thermal stresses.

OXYGEN ENRICHMENT. LN2 is cold enough to condense the surrounding air into a liquid form. The concentration of O_2 in this condensed air is enhanced. This condensed "liquid air" can be observed dripping from the outer surfaces of uninsulated/nonvacuum jacketed lines carrying LN2. This "liquid air" will be composed of > 50% O_2, and will amplify any combustion/flammable hazards in the surrounding areas. Open Dewars of LN2 can condense O_2 from the air into the LN2 and cause an O_2 enrichment of the liquid, which can reach levels as high as 80% O_2. Air should be prevented from condensing into LN2 by the use of loose-fitting stoppers or covers that still allow for the venting of LN2 off-gas. Large quantities of LN2 spilled onto oily surfaces (such as asphalt) could condense enough O_2 to present a combustion hazard. In some cases, such as a large-volume LN2 spill onto asphalt, the surface can become saturated with condensed oxygen and can be shock sensitive (can detonate when shocked). LHe and LH2 can also condense air into the liquid or even the solid phase with an enriched O_2 content. Use O_2 monitors to maintain an O_2 level between 19.5% and 23.5%.

LN2/IONIZING RADIATION FIELD. A unique hazard can result from the use of LN2 in high ionizing radiation fields where the generation of O_3 or NO_x may cause a potential explosion hazard when the LN2 has condensed quantities of O_2 from the atmosphere. The applicable control measure is to minimize the accumulation of O_2 into the LN2 and to keep containers free of hydrocarbon contamination.

NOISE TRANSFER. Venting of cryogens can generate, in some cases, noise levels that could require hearing protection. Sound levels in excess of 150 dBA have been recorded during routine tank filling. A redesign of the equipment or procedure could also be addressed in these cases.

ACCIDENTAL RELEASES/SPILLS (OR OVERFLOWS). Accidental releases/spills (or overflows) of LN2 can present hazards and cause property damage as noted in the hazards discussed above. This most often is a result of inadequate training on the specific hazards and procedures. These releases can come from automated level control systems, but more frequently are the result of manual operations left unattended. The level of concern over these releases increases with the volume of the cryogen source. House LN2 systems represent very large quantities with the potential for release. Separate (stand-alone) supply Dewars are inherently safer in this respect because they have smaller volumes. Releases into the building or lab space are the most hazardous, presenting the primary hazards of asphyxiation, personnel exposure, and property damage may result from significant releases of LN2. When spilled on a surface, cryogens spread as far as the quantity of liquid spilled and the physical confines of the area allow. Their vapors spread even further and can present a hazard to personnel some distance away from the release/spill.

RELEASES INTO BUILDING EXHAUST SYSTEMS. Releases into building exhaust systems also can present significant hazards. These releases typically occur when the operator opens a bypass valve in an attempt to precool the piping to LN2 temperatures and then mistakenly leaves the bypass valve open. These releases can adversely affect the normal operation of the building’s exhaust system or can cause the exhaust system to fail and release significant quantities of LN2 into the building’s air space.

ACCIDENTS CAUSED BY EQUIPMENT FAILURE (equipment not designed for cryogenic service.) Cryogenic fluids should only be handled in apparati specifically designed for that purpose. Accidents frequently occur where equipment not designed for cryogenic service is used, such as when a consumer-rated Thermos® bottle is used for LN2 or Dry Ice. Over pressure and resultant rupture of the container is frequently the result. These types of accidents can also occur when cryogenic-rated equipment is inappropriately modified and the original safe venting design is compromised.

LIFTING. Physical studies of accident statistics involving cryogenics will always include back strains or other lifting injuries associated with Dewars. Although this hazard is not specifically cryogenic in nature, it is appropriate to note this as a hazard associated with cryogenic applications. Be careful when lifting and moving cryogenic Dewars. The proper use of carts or hand trucks can help prevent these injuries. Alternately, the use of low-pressure liquid transfer equipment and procedures can replace lifting and pouring operations.

BACK INJURIES. Back injuries may result from lifting cryogenic liquid Dewars. Dewars of LN2 or LHe may be accidentally tipped over when crossing obstructions, such as door thresholds. Handle these Dewars with the appropriate care and on the appropriate floor surfaces. Maintain the general condition (wheels, handles, etc.) of the Dewars in proper functioning condition.

OTHER. Specific cryogenic fluids will present specific hazards in addition to the above concerns. Examples include:

- LOX and the additional hazards of enhanced combustion, with materials compatibility and cleanliness (hydrocarbon contamination) as added concerns. Do not smoke or allow ignition sources near LOX. LOX is also shock-sensitive. If it spills, do not walk or roll equipment over the spilled area for 30 minutes until the vapors clear. If any clothing is soaked with LOX, remove it immediately and let it air for at least 60 minutes. Keep it away from any ignition sources.
- LH2 and the additional hazards of flammability and materials embrittlement, with the added concerns of low ignition energy, proper bonding and grounding of equipment, and venting of off-gases. Do not smoke or allow ignition sources near LH2. Ground all electrical equipment according to NFPA 50B or National Electrical Code Article 500 (see References). Allow LH2 off-gassing to a suitable location, preferably outdoors. Do not transfer LH2 from one container to another in an air atmosphere; if you do, then LOX will condense with LH2 and create an explosion hazard. Do not spill LH2, since you will create a flammable vapor cloud. Monitor any areas where you use LH2 with a flammable gas detector.
- Toxicity concerns of CO and F_2.

Handling and Personal Protective Equipment

1. Familiarize yourself with the hazards of cryogenic fluids before working with them. Ask an experienced user to show you how to operate Dewars or other cryogenic containers.

2. Wear a full face shield over safety glasses to protect your eyes.

3. Wear loose-fitting thermal insulated or leather gloves. If they become saturated with a cryogen, you can remove them quickly. Insulated gloves do **not** allow you to immerse you hands in a cryogen; they are for immediate protection only.

4. As always, wear long sleeves, long pants, and completely-closed shoes. If you are moving Dewars, you should wear safety shoes.

5. Always handle cryogens carefully. Their extremely low temperatures can produce cryogenic burns and freeze underlying tissue. Exposure to their cold vapors can damage your eyes.

6. Always stand clear of boiling vapors or splashed liquids. Boiling and splashing always occur when placing a room-temperature object inside the cryogen and pouring the cryogen into a room-temperature container, so do these operations slowly. Use tongs to place and remove objects inside cryogens.

7. Do not touch uninsulated pipes or containers with unprotected hands.

8. Never use polystyrene boxes for cryogen storage or transport.

9. **Never accompany a transport Dewar in an elevator**. The same procedure to be followed when moving gas cylinders between floors holds for cryogenic fluids transport. Any internal transport involving the use of elevators requires the presence of two people: the first person puts the transport Dewar in the empty elevator and sends the elevator to the destination floor. S/He will not accompany the Dewar. At the receiving end a second person will take the Dewar from the elevator and move it to its final destination.

First Aid

DERMAL EXPOSURE. Remove any clothing that may restrict circulation to the affected area. Do not rub frozen tissue. Instead place the affected area in a warm (not hot; < 105°F/40°C) water bath. Do not use dry heat. Seek medical attention immediately. Frozen tissue is usually not painful, but can have a waxy or yellowish appearance. When thawed it will be swollen, painful, and prone to infection. Cover the thawed area with a dry sterile dressing and protect it with bulky clothing pending medical attention. If large areas of your body are affected, remove your clothing, take a warm shower, and get medical attention immediately.

OCULAR EXPOSURE. Your eyes may be frostbitten. Warm them in a water bath (not hot; < 105°F/40°C) and seek medical attention immediately.

HYPOTHERMIA. In this case, warm the person slowly to avoid shock. Seek medical attention immediately.

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References/For More Information

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http://www.chem.kuleuven.ac.be/safety/info20.htm

http://www.sandia.gov/bus-ops/scm/esh/Sand2007_5296_W_SafeHandlingofCryogenicFluids.pdf

http://www.dryiceinfo.com/

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