Cryogenic Liquids and their Hazards

What are cryogenic liquids?

Cryogenic liquids are liquefied gases that are kept in their liquid state at very low temperatures. The word "cryogenic" means "producing, or related to, low temperatures," and all cryogenic liquids are extremely cold. Cryogenic liquids have boiling points below -150°C (- 238°F) (Carbon dioxide and nitrous oxide, which have slightly higher boiling points are sometimes included in this category). All cryogenic liquids are gases at normal temperatures and pressures. These gases must be cooled below room temperature before an increase in pressure can liquefy them. Different cryogens become liquids under different conditions of temperature and pressure, but all have two properties in common: they are extremely cold, and small amounts of liquid can expand into very large volumes of gas.

The vapours and gases released from cryogenic liquids also remain very cold. They often condense the moisture in air, creating a highly visible fog. In poorly insulated containers, some cryogenic liquids actually condense the surrounding air, forming a liquid air mixture. Cryogenic liquids are classified as "compressed gases" according to WHMIS criteria. Details of these criteria can be found in the Controlled Products Regulations.

Everyone who works with cryogenic liquids (also known as cryogens) must be aware of their hazards and know how to work safely with them.

Please see the OSH Answers How Do I Work Safely with Cryogenic Liquids? for more information.

What are the different types of cryogenic liquids?

Each cryogenic liquid has its own specific properties but most cryogenic liquids can be placed into one of three groups:

- **Inert Gases**: Inert gases do not react chemically to any great extent. They do not burn or support combustion. Examples of this group are nitrogen, helium, neon, argon and krypton.

- **Flammable Gases**: Some cryogenic liquids produce a gas that can burn in air. The most common examples are hydrogen, methane and liquefied natural gas.
- **Oxygen**: Many materials considered as non-combustible can burn in the presence of liquid oxygen. Organic materials can react explosively with liquid oxygen. The hazards and handling precautions of liquid oxygen must therefore be considered separately from other cryogenic liquids.

How are cryogenic liquids contained?

Cryogenic liquids are shipped and used in thermally insulated containers. These cryogenic liquid containers are specifically designed to withstand rapid temperature changes and extreme differences in temperature.

Liquid Dewar Flasks

Liquid dewar flasks are non-pressurized, vacuum-jacketed vessels, somewhat like a "Thermos bottle". They should have a loose fitting cap or plug that prevents air and moisture from entering, yet allows excess pressure to vent. Flasks containing helium, hydrogen and other low- boiling liquids have an outer vessel of liquid nitrogen for insulation.

Laboratory Liquid Dewar Flasks

Laboratory liquid dewars have wide-mouthed openings and do not have lids or covers. These small containers are primarily used in laboratories for temporary storage.

Liquid Cylinders

Liquid cylinders are pressurized containers specifically designed for cryogenic liquids. This type of container has valves for filling and dispensing the cryogenic liquid, and a pressure-control valve with a frangible (bursting) disk as backup protection. There are three major types of liquid cylinders which are designed for dispensing:

- liquid or gas
- only gas
- only liquid

What are the health hazards of cyrogenic liquids?

There are three groups of health hazards associated with cyrogenic liquids: extreme cold, asphyxiation, and toxicity.

Extreme Cold Hazard

Cryogenic liquids and their associated cold vapours and gases can produce effects on the skin similar to a thermal burn. Brief exposures that would not affect skin on the face or hands can damage delicate tissues such as the eyes. Prolonged exposure of the skin or contact with cold surfaces can cause frostbite. The skin appears waxy yellow. There is no initial pain, but there is intense pain when frozen tissue thaws.

Unprotected skin can stick to metal that is cooled by cryogenic liquids. The skin can then tear when pulled away. Even non-metallic materials are dangerous to touch at low temperatures. Prolonged breathing of extremely cold air may damage the lungs.

Asphyxiation Hazard

When cryogenic liquids form a gas, the gas is very cold and usually heavier than air. This cold, heavy gas does not disperse very well and can accumulate near the floor. Even if the gas is non-toxic, it displaces air. When there is not enough air or oxygen, asphyxiation and death can occur. Oxygen deficiency is a serious hazard in enclosed or confined spaces.

Small amounts of liquid can evaporate into very large volumes of gas. For example, one litre of liquid nitrogen vapourizes to 695 litres of nitrogen gas when warmed to room temperature (21°C).

Toxic Hazards

Each gas can cause specific health effects. For example, liquid carbon monoxide can release large quantities of carbon monoxide gas, which can cause death almost immediately. Refer to the safety data sheet for information about the toxic hazards of a particular cryogen.

What are the flammability hazards of cyrogenic liquids?

Several types of situations exist that may result in a flammability hazard including: fire, oxygen-enriched air, liquid oxygen, and explosion due to rapid expansion.

Fire Hazard

Flammable gases such as hydrogen, methane, liquefied natural gas and carbon monoxide can burn or explode. Hydrogen is particularly hazardous. It forms flammable mixtures with air over a wide range of concentration (4 percent to 75 percent by volume). It is also very easily ignited.

Oxygen-Enriched Air

Liquid hydrogen and liquid helium are both so cold that they can liquefy the air they contact. For example, liquid air can condense on a surface cooled by liquid hydrogen or helium. Nitrogen evaporates more rapidly than oxygen from the liquid air. This action leaves behind a liquid air mixture which, when evaporated, gives a high concentration of oxygen. This oxygen-enriched air now presents all of the same hazards as oxygen.

Liquid Oxygen Hazard

Liquid oxygen contains 4,000 times more oxygen by volume than normal air. Materials that are usually considered non-combustible, (such as carbon and stainless steels, cast iron, aluminum, zinc and teflon (PTFE),) may burn in the presence of liquid oxygen. Many organic materials can react explosively, especially if a flammable mixture is produced. Clothing splashed or soaked with liquid oxygen can remain highly flammable for hours.

Explosion Due to Rapid Expansion

Without adequate venting or pressure-relief devices on the containers, enormous pressures can build up. The pressure can cause an explosion called a "boiling liquid expanding vapour explosion" (BLEVE). Unusual or accidental conditions such as an external fire, or a break in the vacuum which provides thermal insulation, may cause a very rapid pressure rise. The pressure relief valve may not be able to handle this increased pressure. Therefore, the containers must also have another backup device such as a frangible (bursting) disc.

Canadian Center for Occupational Health and Safety

Liquid Nitrogen BLEVE video:

http://www.dailymotion.com/video/xlaw7k_extreme-science-liquid-nitrogen-demo_lifestyle

BLEVE Explanation:

http://www.youtube.com/watch?v=UM0jtD_OWLU&NR=1&feature=endscreen