BOC

A Member of The Linde Group

Care with Cryogenics.

Your Guide to Working with Cryogenic Liquids.

Contents.

1. What are Cryogenics?

Liquefied atmospheric gases may be referred to as cryogenic liquids. These gases are liquefied by cooling to low temperatures. There are a number of potential hazards when using cryogenics.

This document highlights these hazards, the causes and the appropriate precautions.

2. Properties of Cryogenic Liquids.

The gases covered in this document and their physical properties are detailed in the table below. All gases are non-flammable, although liquid oxygen is an oxidant and can promote vigorous combustion of many materials.

Property	Oxygen (O_2)	Nitrogen (N_2)	Argon (Ar)	Helium (He)	Carbon Dioxide (CO_2)
Molecular Weight	32	28	40	4	44
Colour of gas	None	None	None	None	None
Colour of liquid	Light Blue	None	None	None	None
Normal boiling point at atmospheric pressure (°C)	-183	-196	-186	-269	-78.5 (sublimes)
Ratio of volume gas to volume of liquid (measured at 15°C and absolute pressure of 1 atm)	844	680	824	738	845 (solid)
Relative density of gas at atmospheric pressure and 15°C (Air =1)	1.103	0.967	1.39	0.138	1.53
Liquid density at boiling point and atmospheric pressure (kg/m^3)	1142	806	1395	125	1564 (solid)
Latent heat of evaporation at boiling point (kJ/kg)	213	199	162	21	573 (sublimation)

3. Hazards of Cyrogenics.

3.1 Cold burns, frostbite and hypothermia.

Cold burns and frostbite.

Because of the low temperatures of liquefied atmospheric gases, the liquid, cold vapour or gas can produce damage to the skin similar to heat burns. Unprotected parts of the skin coming into contact with uninsulated items of cold equipment may also become stuck to them and the flesh may be torn on removal.

Cold vapours or gases from liquefied atmospheric gases may cause frostbite, given prolonged or severe exposure of unprotected parts. A symptom that usually gives warning of freezing is local pain, however sometimes no pain is felt or it is short lived. Frozen tissues are painless and appear waxy, with a pale yellowish colour. Thawing of the frozen tissue can cause intense pain. Shock may also occur.

Treatment of cold burns.

The immediate treatment is to loosen any clothing that may restrict blood circulation and seek hospital attention for all but the most superficial injuries. Do not try to remove clothing that is frozen to the skin. Do not apply direct heat to the affected parts, but if possible place in lukewarm water. Clean plastic kitchen film or sterile dry dressings should be used to protect damaged tissues from infection or further injury, but they should not be allowed to restrict the blood circulation. Alcohol and cigarettes should not be given.

Where exposed skin is stuck to cold surfaces such as uninsulated cryogenic pipe work, isolate the source of the cold liquid and thaw with copious amounts of tepid water until the skin is released.

Effect of cold on lungs.

Transient exposure to very cold gas produces discomfort in breathing and can provoke an asthma attack in susceptible people.

Hypothermia.

Low air temperatures arising from the proximity of liquefied atmospheric gases can cause hypothermia and all people at risk should wear warm clothing.

Typical symptoms of hypothermia are:

- A slowing down of physical and mental responses.
- Unreasonable behaviour or irritability.
- Speech or vision difficulty.
- Cramps and shivers.

Treatment of hypothermia.

People appearing to be suffering from hypothermia should be wrapped in blankets and moved to a warm place. Remove any wet clothing that is not frozen to their skin. Seek immediate medical attention. No direct form of heating should be applied except under medical supervision.

3.2 Asphyxiation.

The evaporation of inert cryogenic liquids may, in evaporating, produce oxygen-deficient atmospheres, which will result in asphyxiation if breathed. Atmospheres containing less than 10% oxygen can produce brain damage and perhaps death.

It is essential to ensure that, if any cryogenic liquid is used in open vessels or vessels venting into the atmosphere, there will be adequate ventilation and, if necessary, atmospheric analysis is done at regular intervals and permanent monitoring is installed.

3.3 Fire Hazard.

If the atmosphere is enriched with oxygen the likelihood and potential intensity of fire is increased. Combustible materials that are not usually combustible in air will burn fiercely in an enriched atmosphere. Clothing saturated with oxygen will burn vigorously with potentially fatal results.

In all cases, good ventilation should be provided to minimise the risk. As oxygen vigorously supports combustion, it is not usually possible to extinguish an oxygen-fed fire using conventional means. The first essential step in extinguishing such a fire is to eliminate the source of supply of the oxygen. Conventional methods may then be employed as necessary.

3.4 Dense cold vapour.

Due to the relatively high density of the cold vapour of the liquids, the gases may collect and persist in low lying areas, posing an oxygen deficiency or enrichment hazard. Manholes, trenches, basements, drainage systems, underground service ducts and any low lying, poorly ventilated areas may pose such a hazard. Entry into these areas should be controlled by systems such as signage, monitoring and Permit to Work.

3.5 Liquid air condensation.

Whilst nitrogen and helium appear to be safe from the risk of combustion because they are inert, these liquids are cold enough at normal boiling points to condense oxygen from the atmosphere. This produces higher oxygen content than normal air, increasing the risk of combustion. It is therefore essential that the vessel is properly insulated. It is also recommended to exclude combustible insulating materials from liquid nitrogen and helium systems and installations. Liquid argon and carbon dioxide cannot condense oxygen from the atmosphere.

3.6 Over pressurisation.

When vaporised into gas, all of these liquefied gases increase many hundreds of time in volume. This results in a large pressure increase if the volume change is restricted. The normal in leak of heat through the insulated walls of the storage vessels and pipe work into the cryogenic liquid raises its temperature and hence, the pressure rises due to the generation of gas.

Cryogenic systems must therefore be designed with adequate pressure relief on storage vessels and anywhere where liquid may be trapped, such as pipe work between valves.

If liquid is vented into the atmosphere, it vaporisers with a consequential large expansion in volume which can be very noisy. Therefore, venting should be controlled and adequate precautions taken to protect personnel. Liquid should not be vented in an enclosed space.

3.7 Embrittlement.

The most significant consideration when selecting equipment and materials for low temerpature use is that of possible brittle fracture. Carbon steel is extremely brittle at the cryogenic temperatures of liquid nitrogen, argon and oxygen. (Certain types of carbon steel can be used with liquid carbon dioxide because it is relatively warm in comparison to liquid nitrogen, argon and oxygen). Metals used in any equipment should satisfy the impact test requirements of the design code being used.

If there is a change in the use of a plant from its original design, it may result in the liquid usage rate exceeding the capacity of the vaporising equipment. This can cause cryogenic liquid to reach parts of the equipment that were not originally intended for low temperature conditions, increasing the risk of potential brittle fracture.

Low temperature safety shut off systems or flow restrictions, should be considered where excess flow is possible.

4. Causes and Avoidance of Exposure.

4.1 Contact with cold surfaces.

Where possible insulate all exposed cold surfaces using suitable materials.

4.2 Splashes and spillages.

→ Use suitable PPE (see section 5.2).
→ Use appropriate manual handling equipment when moving vessels containing cryogenic liquids.
→ Report all leaks immediately to site emergency response, emergency services and BOC Customer Engineering Services.

4.3 Prolonged exposure to low temperature environments.

→ Use suitable insulating PPE.
→ Minimise time of exposure.

4.4 Inadequate design/incorrect choice of materials.

→ Only use competent system designers.
→ Only use approved materials. Conduct regular planned preventative maintenance.
→ Do not exceed the flow rate specified for the equipment.
→ Comply with relevant design standards.

5. Preventative Measures.

5.1 Information and training.

All people who work with low temperature liquefied gases or systems using such gases should be given adequate training on the risks of asphyxiation, fire hazards, cold burns, frostbite and hypothermia. Special attention should be drawn to the insidious nature of the risks due to the rapidity of the effects, coupled with the fact than an operator may be completely unaware that a hazardous condition has developed. Fire response procedures, including locations of shut off points, must be in place and training conducted.

5.2 Protective clothing.

Protective clothing is only intended to protect the wearer handling cold equipment from accidental contact with liquefied atmospheric gases or parts in contact with it. Non-absorbent leather or insulated gloves should always be worn when handling anything that is, or has been recently, in contact with cryogenic liquids. The gloves should be a loose fit so that they can easily be removed if liquid should splash onto or into them. Gauntlet gloves are not recommended because liquid can easily splash into the wide cuff.

It is essential that clothing is kept free of oil and grease where oxygen is in use.

If clothing becomes contaminated with liquefied atmospheric gases or their vapour, the wearer should ventilate it for a minimum of 15 minutes whilst walking around in a well-ventilated area. The risk with contamination by liquid oxygen is the rapid burning of the material, even when started via a tiny ignition source (a spark or a piece of burning tobacco). Therefore, in these circumstances it is essential to ventilate clothing for at least 15 minutes (or replace it) and to keep away from any such source of ignition.

Woven materials are best avoided, but if they are used for protective clothing it is essential to ensure that they do not become saturated with cold liquid or gaseous oxygen.

Goggles or a facemask should be used to protect the eyes and face when carrying out operations where spraying or splashing of liquid may occur. Long sleeved clothing should be worn. These should be without open pockets or turn-ups where liquid could collect. Trousers should be worn outside boots for the same reason.

A person whose clothing catches fire should be deluged with water from a shower hose or series of fire buckets and moved into the fresh air as soon as possible. It is very dangerous to attempt to resue a person catching fire in an oxygen-enriched atmosphere as the rescuer is likely to catch fire as well. Emergency response procedures should be developed and personnel trained.

5.3 Warning signs.

Where ever cryogenic gases are used or stored, hazard warning signs should be displayed as necessary and barriers placed indicating the extent of the hazard. Any pictogram used should comply with Australian regulation AS 1319.

BOC Bulk Vessels.

6. Dewars.

Safe working procedures must be developed and adhered to for the use of dewars, including their transportation within and around the premises. Special safety procedures are necessary when carrying filled dewars in lifts. Only use dewars that are correctly and clearly labelled. Always ensure that adequate ventilation is provided in areas where dewars are filled, used or stored.

Adequate emergency procedures must be in place in the event of a liquid spillage, cold burn or suspected asphyxiation.

Ice plugs can form in the neck of dewars and can be ejected at high velocity due to pressure build up. Avoid them by ensuring that protective caps are always used and that dewars are fully emptied before being taken out of use or put into storage.

7. Customer Engineering Services.

BOC's CES team of expert engineers and project managers are readily available to assist with any gas related solution. With over 60 years experience in gas and associated industries and access to global resources, we provide expert technical capability.

BOC is committed to providing the kind of support and customer service that you would expect from Australia and New Zealand's largest gases company.

With a strong presence throughout Australia and New Zealand and 24 hour support from qualified technicians, CES can provide comprehensive on-going maintenance and service support for both BOC and customer owned equipment. We can also offer expert training and safety, design and process audits to suit specific customer needs.

Our CES team is on hand to help you with your Cryogenic liquid requirements.

For information about using cryogenic liquids contact our Customer Engineering Services team:

CES Australia
1800 624 006

CES New Zealand
0800 500 886

Emergency Response Line

Australia
1800 653 572

New Zealand
0800 500 886

For more information on any BOC products or services contact the BOC Customer Service Centre on:

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131 262
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