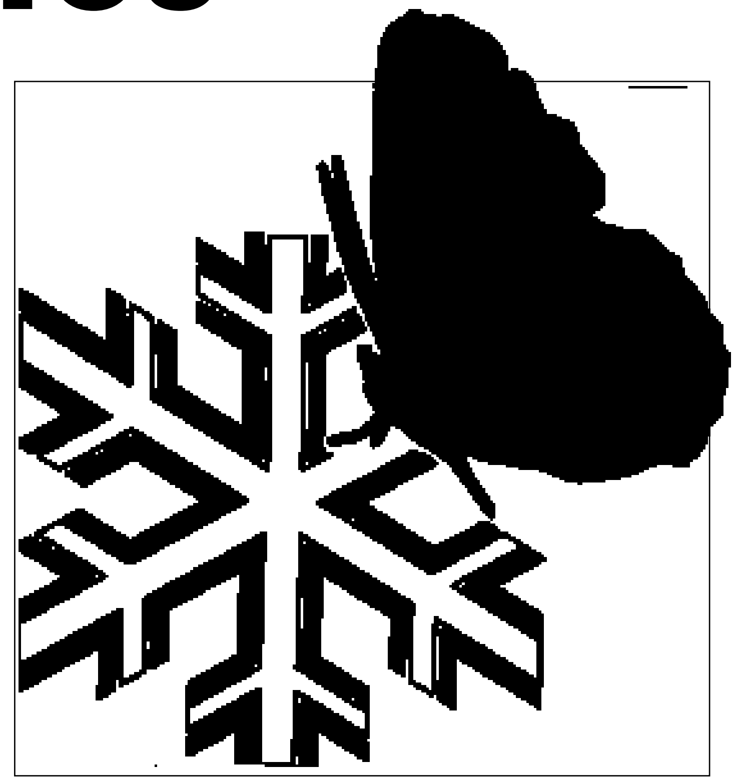
Care with cryogenics



BOC GASES

The safe use of low temperature liquefied gases

Care with cryogenics

Index

Liquefied gases – oxygen, nitrogen, argon, helium and carbon dioxide

I INTRODUCTION

1.1 OBJECTIVE

The purpose of this publication is to give users of BOC low temperature liquefied gases information on their properties, the hazards associated with their use and simple precautions to be taken to ensure they are used safely. Detailed safety information for individual gases is provided in data and safety sheets supplied by BOC.

1.2 GASES CONSIDERED AND TYPICAL USES

Low temperature liquefied atmospheric gases, sometimes known as cryogenic liquids, are stored in convenient concentrated form and are safely used in large quantities by industry.
BOC delivers liquid nitrogen, oxygen, argon and carbon dioxide into vacuum insulated evaporators (VIEs) and the customer does not have to handle the liquid or operate any valves on the equipment. The gases can be used for a multitude of different applications. These include food freezing and chilling, water treatment, chemical processes, metal fabrication, heat treatment, cold processes and electronics. Liquid helium is supplied in portable dewars for specialist applications such as nuclear magnetic resonance spectrometry in the medical field. Liquid nitrogen, argon and oxygen are also supplied in smaller portable vacuum insulated vessels by BOC's Cryospeed service.

2 PROPERTIES OF LOW TEMPERATURE LIQUEFIED ATMOSPHERIC GASES

The hazards associated with the low temperature liquefied gases relate to their physical properties.
Some physical properties of the five liquefied atmospheric gases covered by this leaflet are given in Table 1.
All five gases are odourless and non-flammable in air.
Carbon dioxide has a distinctive taste in high concentrations (10%) but the others are tasteless.

TABLE 1

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 liquidLight 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 101.3kPa	842	682	822	738	845 (solid)
Relative density of gas at 101.3 kPa (Air = 1)	1.105 @25°C	0.967 @25°C	1.380 @0°C	0.138 @0°C	1.48 @25°C
Liquid density at absolute pressure of 101.3 kPa (kg/m^3)	1141	807	1394	125	
Latent heat of evaporation (kj/kg)	213	199	161	20	573 (sublimination)

3 HAZARDS

The hazards arising from the use of lov.~ temperature liquefied gases are:

1. Asphyxiation in oxygen deficient atmospheres
2. Fire in oxygen enriched atmospheres
3. Cold burns, frostbite and hypothermia from the intense cold
4. Overpressurisation from the large volume expansion of the liquid

3. 1 ASPHYXIATION

3.1.1 Nitrogen, argon and helium

Nitrogen, argon and helium may produce local oxygen-deficient atmospheres, which will produce asphyxia if breathed. This is especially true in confined spaces. Atmospheres containing less than 18% oxygen are potentially dangerous and entry into atmospheres containing less than 20% is not recommended. Atmospheres containing less than 10% oxygen can result in brain damage and death.

3.1.2Carbon Dioxide

Carbon dioxide is essentially an asphyxiant gas with only mild toxic properties and no cumulative effects. The Health and Safety Executive Guidance Note EH 40— Occupational Exposure Limits indicates that the recommended exposure limit for carbon dioxide is 5,000 ppm (0.5%) by volume calculated as an eight hour time-weighted average concentration in air, or 15,000 ppm (1.5%) for a 15 minute period.

Carbon Dioxide content (vol%)	Effects and symptoms
2-4%	Slight feeling of suffocation and an increased breathing rate.
5%	Headaches, dizziness and sweating can occur after 30 minute exposure.
5-9%	Breathing becomes laboured, judgement impaired
9%	Fatal on exposures of about four hours.
12%	Immediate unconsciousness and fatality may occur after a few minutes

It is important to note that individuals can react at different rates. Atmospheres containing less than 20% oxygen or more than 0.5% carbon dioxide should not be entered.

3.1.3 Oxygen deficiency

Asphyxia due to oxygen deficiency is often rapid with no prior warning to the victim. A general indication of what is liable to happen in oxygen deficient atmospheres is given in the table below, but it should be appreciated that the reactions of some individuals may be very different from those shown.

Oxygen content (vol%)	Effects and symptoms (at atmospheric pressure)
11-14	Diminution of physical and intellectual performance without person's knowledge
8-11	Possibility of fainting after a short period without prior warning
6-8	Fainting within a few minutes, resuscitation possible if carried out immediately
0-6	Fainting almost immediate, death ensues, brain damage even if rescued

Symptoms of the possible onset of asphyxia can include:

i) Rapid and gasping breathing
ii) Rapid fatigue
iii) Nausea
iv) Vomiting
v) Collapse or inability to move
vi) Unusual behaviour

Victims may well not be aware of their condition. If any of these symptoms appear in situations where asphyxia is possible, affected individuals need to be moved to the open air immediately and followed up with artificial respiration if necessary. HOWEVER, attempts to rescue people from confined spaces or where oxygen deficient atmospheres may well be present should only be made by those trained in the use of AND wearing breathing apparatus and familiar with confined space entry procedures - refer to HSE Guidance Note GS5 "Entry into Confined Spaces."

3.2 FIRE HAZARDS FROM OXYGEN ENRICHED ATMOSPHERES

3.2.1

If the atmosphere is enriched with oxygen the likelihood and potential intensity of fires is increased. Many materials not usually combustible in air will burn fiercely in an oxygen enriched atmosphere. They can also be ignited with minimum energy sources that would not, in air, be considered sufficient. Smoking must, therefore, be prohibited in the vicinity of liquid oxygen and suitable warning notices displayed.

3.2.2

Smoking should also be prohibited in the vicinity of liquid helium and when large quantities of liquid nitrogen are being used for such processes as shrink fitting in view of the possibility of localised atmospheric enrichment with oxygen. In all cases, good ventilation should be provided.

3.2.3

Oxygen reacts with most elements. The initiation, speed, vigour and extent of these reactions depend in particular upon:

— The concentration, temperature and pressure of the reactants.

— Ignition energy and mode of ignition

In certain circumstances detonations can occur.

3.2.4

Oil and grease are particularly hazardous in the presence of oxygen as they can ignite spontaneously and burn with explosive violence. They should never be used to lubricate oxygen or enriched air equipment.
(Special lubricants which are compatible with oxygen can be used under certain conditions.)

3.2.5

In the event of a release of liquid or cold gaseous oxygen, a white mist usually forms due to the condensation of atmospheric moisture and this indicates the approximate extent of the area of oxygen enrichment. Although fire may not be involved, the chance of accidental ignition can be reduced by the use of water fog which helps to dissipate the oxygen.

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.

3.3 COLD BURNS, FROSTBITE AND HYPOTHERMIA

3.3.1 Cold burns

Because of the low temperature of liquefied atmospheric gases the liquid or even cold vapour or gas can produce damage to the skin similar to heat burns. Unprotected parts of the skin coming in contact with uninsulated items of cold equipment may also stick fast to them and the flesh may be torn on removal.

3.3.2 Frostbite

Cold vapours or gases from liquefied atmospheric gases may cause frostbite given prolonged or severe exposure of unprotected parts. A symptom is local pain which usually gives warning of freezing but sometimes no pain is felt or it is shortlived. 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.

The immediate treatment is to loosen any clothing that may restrict blood circulation and seek immediate hospital attention for all but the most superficial injuries. Do not apply direct heat to the affected parts, but if possible place in lukewarm water. 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 be given.

3.3.3 Effect of cold on lungs

Transient exposure to very cold gas produces discomfort in breathing and can provoke an attack of asthma in susceptible people. Prolonged inhalation of very cold vapour or cold gas, whether respirable or not, is unlikely to produce damage to lungs unless the temperature is so low that the mouth and nose are frostbitten.

3.3.4 Hypothermia

Low air temperatures arising from the proximity of liquefied atmospheric gases can cause hypothermia and all people at risk should be warmly clad. Hypothermia is possible in any environment below 1 0°C but susceptibility depends on length of exposure, atmospheric temperature and, not least, the individual; older people are more likely to be affected.

The symptoms of hypothermia are:

i) A slowing down of physical and mental responses
ii) Unreasonable behaviour or irritability
iii) Speech or vision difficulty
iv) Cramp and shivers

People apparently suffering from hypothermia should be wrapped in blankets and moved to a warm place. Seek immediate medical attention. No direct form of heating should be applied except under medical supervision.

4 SOURCES OF OXYGEN ENRICHMENT AND DEFICIENCY

4. 1

Oxygen enrichment or deficiency may occur in any situation where the liquefied gases or the gases themselves are being used, transported or stored without the appropriate engineering or procedural controls in place.

4.2

The process itself may inherently give rise to large volumes of cold or hot gas which may produce oxygen deficient atmospheres unless the appropriate engineering controls such as containment, or local or general ventilation are applied. Examples are:

— Inert atmosphere treatment processes
— Cryogenic liquid immersion processes, eg shrink fitting
— Food freezing and chilling processes

4.3

The gas may be used for inerting purposes such as inert blankets for plant and equipment in which flammable liquids or potentially explosive dusts are present. The absence of procedural controls, such as Permits to Work for entry into such plant and equipment will pose an asphyxiation hazard.

4.4

Vents and emergency relief devices which vent into the building may cause local oxygen enrichment or deficiency.

4.5

Leaks of gas or spillage of liquid may cause local oxygen enrichment or deficiency.

4.6

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

5 PREVENTIVE MEASURES

5.1 INFORMATION AND TRAINING

All people who work with low temperature liquefied gases or systems using such gases should be given adequate instruction as to the risk 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 that an operator may be completely unaware that a hazardous condition has developed.

Practical training should be given in the means by which such risks can be minimised and the actions to be taken in an emergency.

5.2 PERMITS TO WORK

5.2. 1

Any Work which has to be carried out in circumstances where there may be an oxygen deficient or enriched atmosphere must be controlled by a Permit to Work system which should address:

i) Monitoring of the work area for oxygen deficiency or enrichment
ii) Physical isolation of the work area from sources of oxygen deficiency or enrichment and other hazards
iii) The need for the use of suitable breathing apparatus
iv) The provision of life lines, belts, harnesses and suitable rescue equipment

Due to the relatively high density of the cold vapour of the liquids, the gases may collect and persist in areas which may not be immediately recognisable as confined spaces 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 and entry into these areas should be controlled by a Permit to Work.

There are many fixed, portable and personal oxygen monitors commercially available. There are also fixed and portable carbon dioxide monitors available. Suitable ones should be chosen for the particular circumstances to monitor the area before entry and whilst work is in progress. The monitors should be calibrated regularly and be routinely maintained.

Physical isolation of plant and equipment from oxygen or inert gas pipelines should not rely solely on the closure of valves. In addition a section of pipe should be removed or a blanking spade or spectacle plate should be inserted into the pipeline.

5.2.5

People who are required to use breathing apparatus and rescue equipment should be medically fit to do so, should be trained in its use and should receive annual refresher training. The breathing apparatus should be routinely maintained and kept in good working order as should the rescue equipment, ie life lines, belts, harnesses, lifting gear and rescusitation equipment.

5.3 PROTECTIVE CLOTHING

5.3. 1

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 gloves should always be worn when handling anything that is, or has been recently, in contact with liquefied atmospheric gases. The gloves should be a loose fit so that they can easily be removed if liquid should splash onto, or into, them. For this reason, gauntlet gloves are not recommended.

5.3.2

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

5.3.3

If clothing becomes contaminated with liquefied atmospheric gases or vapour, the wearer should ventilate it for a minimum of five minutes whilst walking around in a well ventilated area. With oxygen the risk is of rapid burning of the material; the ignition source may be tiny- a spark or a piece of burning tobacco-and so in these circumstances it is essential to keep away from any such source of ignition.

5.3.4

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.

5.3.5

Goggles, or a face mask, should be used to protect the eves and face where spraying or splashing of liquid may occur. Overalls, or similar clothing should be worn. These should preferably be made without open pockets or turn-ups where liquid could collect. Trousers should be worn outside boots for the same reason.

5.3.6

A person whose clothing catches fire should be deluged with water from a hose or series of fire buckets, and moved into the fresh air as soon as possible. It is very dangerous to attempt to rescue a person catching fire in an oxygen enriched atmosphere, as the rescuer will most probably catch fire himself. (In some cases it may be possible to enter such a space if the rescuer is totally deluged with water and protected by constant water hosing.)

5.4 WARNING SIGNS

Wherever cryogenic gases, particularly oxygen, are stored or used hazard warning signs should be used and, as necessary, barriers placed indicating the extent of the hazard. Any pictogram used should comply with the Health and Safety (Safety Signs and Signals Regulations) 1995 and BS5378.

6 MATERIALS AND EQUIPMENT

6.1 LIQUID NITROGEN, ARGON, OXYGEN AND CARBON DIOXIDE

6.1.I

The BOC VIE used for the storage of cryogenic liquid is specially designed for that purpose. BOC dewars and flasks are likewise specially designed.

6.1.2

The most significant consideration when selecting materials for equipment not specially produced for cryogenic 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 cryogenic carbon dioxide because it is relatively warm. In addition, many materials regarded as safe in air are readily combustible in oxygen-rich atmospheres.

6.1.3

Metals used in any equipment should satisfy the impact test requirements of the design code being used. Equipment for liquid oxygen service must be scrupulously clean as dirt, oil or grease can pose a serious fire or explosion hazard.

6.1.4

With liquid oxygen extreme care must also be taken in the choice of jointing materials which must be compatible with oxygen. Expert advice should be sought. The surface finish can also be important where liquid oxygen or high pressure gaseous oxygen is concerned. Advice on materials can be obtained from BOC.

6.1.5

Whilst liquid nitrogen, argon, helium and carbon dioxide do not promote combustion, it is good practice to use oxygen-compatible materials in these cases as well.

6.1.6

Changes in use of plant from that for which it was designed may result in cryogenic liquid reaching parts which were not originally intended for low temperature conditions.

6.1.7

Whilst nitrogen and helium would appear to be safe from the risk of combustion because they are inert, these liquids are cold enough at normal boiling points to condense air from the atmosphere; this can lead to the production of liquid containing a higher oxygen content than that of air and, consequently, a combustion hazard.

6.1.8

Since there may be condensation of the atmosphere surrounding a vessel containing liquid nitrogen or helium, producing an oxygen-rich atmosphere, it is essential that the vessel is properly insulated. Because of the possibility of oxygen enrichment, it is usual to exclude combustible insulants from liquid nitrogen and helium systems and installations. Liquid argon cannot condense air from the atmosphere.

6.1.9

Many carbon dioxide vessels are not protected by bursting discs as the leak of gas through a ruptured disc would cause excessive evaporation and in turn excessive cooling of the liquid. It would therefore be quite possible for the temperature to fall below the triple point causing solid carbon dioxide to be formed. However for those vessels that are protected by bursting discs, if solid carbon dioxide has formed then the vessel cannot be put back into service by simply replacing the bursting disc, as catastrophic results can occur if liquid carbon dioxide is added to a vessel containing solid carbon dioxide. If you suspect that solid carbon dioxide may have formed, please contact your supplier immediately for advice.

6.2 LIQUID HELIUM

6.2.1

Because of its low boiling point and latent heat of evaporation, liquid helium is supplied in dedicated service dewars which must be handled with care at all times. In particular, liquid helium dewars are designed to exact specifications and should not be used with other liquids whose higher specific gravity might result in failure of the suspension system.

6.2.2

This liquid can only be transferred in vacuum insulated lines and equipment. Even some steels which are satisfactory at liquid nitrogen temperature become brittle in contact with liquid helium.

6.2.3

Any receiving equipment or dewars which have been pre-cooled with liquid nitrogen must be clearly identified and subsequently purged with pure helium gas prior to transfer. Liquid helium can solidify all other known gases and liquids.

6.2.4

The oxygen enrichment hazard is much more significant than with liquid nitrogen. All equipment which may be at liquid helium temperatures must be kept clean to the same standards as liquid oxygen installations.

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