ENVIRONMENTAL HEALTH AND SAFETY

CRYOGENICS GUIDELINES

Cryogenics (also known as liquefied gases) are used for specialty chilling and freezing applications. They find useful applications in chemistry (chemical reactions, chemical reactors), biology (cell lines or vaccines freezing) and instrumentation (magnetic resonance and imaging). There are a number of potential hazards associated with the use of cryogenics. The cryogenics covered in this document and their physical properties are detailed below. Even though most of cryogenics are non-flammable, although liquid oxygen is an oxidant and can promote vigorous combustion of many materials, they can cause severe frost bites and burns or could potentially lead to asphyxiation by displacing oxygen. Anyone who works in laboratories containing cryogenics should familiarize themselves with their SDS and a clear Standard Operating Procedure (SOP) should be established. Therefore, careful precautions should always be taken when handling cryogenics. This document discusses the properties, health and safety hazards, how to properly handle and store cryogenics. Also included are emergency procedures for dealing with accidental cryogenics contact, including first aid treatment information.

❄WARNING❄: The extremely low temperature of cryogenics can cause severe burn-like damage to the skin either by contact with the liquefied gas, surfaces cooled by the fluid or evolving gases. Although most of the cryogenics covered in this document are not flammable, their sudden release from compressed containers can displace oxygen and potentially cause risks of asphyxiation.

1. Properties

A **cryogenic liquid** is a liquid that has a boiling point at or below -150 °C (123 K). Most cryogenic gases are colourless, odourless and tasteless. Some of the properties of common cryogenics are mentioned in Table 1.

Table 1: Properties of cryogenics

Property	Oxygen (O_2)	Nitrogen (N_2)	Argon (Ar)	Helium (He)	Carbon dioxide (CO_2)
Molecular Weight	32	28	40	4	44
CAS #	7782-44-7	7727-37-9	7440-37-1	7440-59-7	124-38-91
Colour of gas	none	none	none	none	none
Colour of liquid	light blue	none	none	none	none
Boiling Point (°C)	-183	-196	-186	-269	-78.5 (sublimes)
Ratio gas / liquid volume	842	682	822	738	845 (solid)
Density (air = 1)	1.105@25°C	0.967@25°C	1.380@0°C	0.138@0°C	1.48@25°C

1. Hazard Classification

WHMIS 1988

Class A: compressed gases (Oxygen, Nitrogen, Argon, Helium, Carbon Dioxide)
Risk of explosion if heated under confinement.

Class C: oxidizing materials (Oxygen)
Contact with combustible material may cause fire.

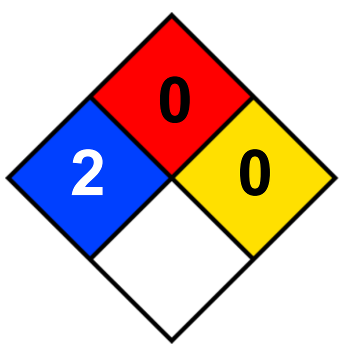
WHMIS 2015

Gas under pressure (Oxygen, Nitrogen, Argon, Helium, Carbon Dioxide)
Simple asphyxiant (Nitrogen, Argon, Helium, Carbon Dioxide)

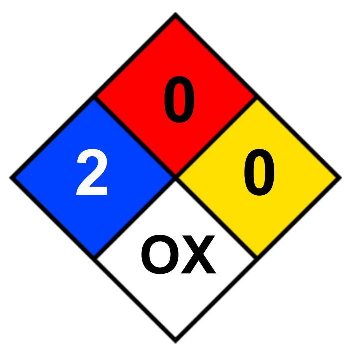
Oxidizing gas (Oxygen)

NFPA

Nitrogen, Helium, Argon



Carbon Dioxide



Oxygen

2. Reactivity, Fire and Explosion Hazards

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 air from the atmosphere. Exposure of combustible materials to oxygen-enriched cryogenic liquids enhances the combustibility of the material. It is recommended to exclude combustible insulating materials from liquid nitrogen and helium systems and installations. Liquid argon is also an inert gas and cannot condense air from the atmosphere. Solid carbon dioxide (dry ice) can neither condense oxygen.

Liquid oxygen vigorously promotes combustion in otherwise non-combustible materials, like carbon and stainless steels, cast iron, aluminum, zinc, and Teflon. It also reacts explosively with organic materials. Prevent all organic substances including oils and greases from contacting liquid oxygen. Thoroughly clean any equipment or container used with liquid oxygen to the degree required for use with oxidizing materials. Some common materials (such as asphalt, kerosene, cloth, wood, paint, tar, and dirt containing oil or grease) can react violently with liquid oxygen at certain pressures and temperatures.

Cryogenic liquids are usually stored in vacuum-insulated vessels. A cryogenic liquid expands by orders of magnitude upon vaporization (see Table 1). For example, one liter of liquid nitrogen becomes 24.6 cubic feet of nitrogen gas. This can cause an explosion of a sealed container. Cryogenic systems must therefore be designed with adequate pressure relief on storage vessels and anywhere where liquid may be trapped, such as pipework between valves. If some liquid is vented into the atmosphere, it vaporises with a consequential large expansion in volume which can be very noisy (hissing sound). Containers may also rupture or explode if exposed to heat.

Soft materials (e.g. rubber and plastics) become brittle when cooled by liquid nitrogen and may shatter unexpectedly.

3. Health Hazards

Cryogenics are extremely cold at atmospheric pressure. Contact with skin may lead to **burns and/or severe frostbites**. 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.
Transient exposure to very cold gas produces discomfort in breathing and can provoke an asthma attack in susceptible people. Furthermore, low air temperatures arising from the proximity of liquefied atmospheric gases can cause **hypothermia**.

Typical symptoms of hypothermia are:

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

While most of cryogenic gases are non-toxic, releasing nitrogen, argon or helium **may produce local oxygen-deficient atmospheres**, which will produce asphyxia if inhaled. As the concentration of inhaled oxygen is reduced from 20.9% to 14% by volume, pulse rate and volume of breathing increase. Table 2 shows the different symptoms of an oxygen deficiency.

Table 2: Oxygen deficiency symptoms

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 if rescued

For example, oxygen depletion resulting from a spill of 50 liters of liquid nitrogen in a room 10m X 8m X 3m is calculated below can be determined using the equation:

$$\frac{100 \times V_O}{V_R}$$

$V_O = 0.209\,(V_R - V_G)$ *for cryogens other than oxygen*
V_R *is the volume of the room*
V_G *is the maximum gas release upon the expansion of the cryogenic liquid*

VR = 10m x 8m x 3m = 240 m^3
VG = 682 x 0.05 m^3 = 34.1 m^3 (1 m^3 = 1000 liters)
VO = 0.209 (VR – VG) = 0.209 (240m^3 – 34.1m^3) = 42.8 m^3
Oxygen Content = (100 x 42.8m^3)/240m^3 = **17.8%**

In oxygen-enriched air, both breathing and the central nervous system may be affected. 80% oxygen for a few hours or 50% for 24 hours does not cause any effect. At pressures above one atmosphere, a condition called hyperoxia appears. Symptoms of hyperoxia include cramps, nausea, dizziness, low body temperature, loss of vision, slow heartbeat, fainting spells, and convulsions which can cause death. Prolonged exposures to greater than 60% oxygen can irritate the mucous membranes.

Carbon dioxide is essentially an asphyxiant gas but also has mild toxic properties. Normal air is 78% nitrogen, 20.9% oxygen and only 0.035% carbon dioxide. **If the concentration of carbon dioxide in the air rises above 0.5%, carbon dioxide can become dangerous**. 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. For these reasons, a carbon dioxide monitor should be used when there is a risk of CO_2 exposure, rather than an oxygen deficiency monitor. Table 3 summarizes the exposure symptoms to carbon dioxide.

Table 3: Carbon dioxide exposure symptoms

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
5-9	Breathing becomes laboured, judgement impaired
9	Fatal after approximately four hours exposure
12	Immediate unconsciousness; fatality may occur after a few minutes

4. Safety Precautions for Cryogenics Use

a) Training

Students and employees who handle cryogenics must have read the Safety Data Sheet (SDS) and receive training on the hazards of cryogenics from their respective department. They must know what to do in the event of a spill or an exposure incident. The SDS must always be kept within the immediate vicinity of the working area along with the Standard Operating Procedure (SOP) developed by the student / employee's department.

b) Ventilation

A poorly or non-ventilated room will be quickly enveloped by the expanding gas from a cryogenic liquid. This will lead to displacement of oxygen and potential asphyxiation of the user. Always use cryogenics in a well-ventilated area, especially when filling a warm container or transfer tube or inserting a warm object, as large volumes of gas are evolved. 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.

c) Eye Protection

Chemical splash goggles for eye protection in combination with a full-length face shield should be used for operations that present splash hazards.

d) Gloves

Hand protection requires thick non-absorbent leather gloves or other gloves developed for protection from extreme cold temperatures (e.g. Cryo-Gloves®). Those gloves are not made for immersion protection; they will only provide short-term protection from accidental contact with the liquid. Check glove manufacturer for recommendations on a suitable glove. 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.

e) Protection Clothing

Wear a lab coat (100% cotton) and closed-toe shoes (non-fabric) or boots with non-slip soles. For operations where spraying or splashing of liquid may occur, overalls or similar 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.

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.

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

No watches, rings or other jewelry should be worn when handling cryogenics, as a splash can freeze these objects to the skin.

f) Hearing Protection

When filling-up Dewar containers with liquefied gases, venting into the atmosphere can occur and can be very noisy (hissing sound). It is always preferable to wear ear muffs or other types of hearing protectors.

g) Safe Work Practice

- Do not directly touch or make contact with cryogenic liquids or uninsulated cryogenic equipment or pipes.
- Do not overfill containers; when pouring or transferring cryogenics, do so slowly to minimize boiling and splashing.
- Only use containers or equipment specified for cryogenic use; 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.
- Exercise caution when adding a cryogenic liquid to a Dewar at room temperature or an object at room temperature to a cryogenic liquid; both will cause the liquid to boil and splash vigorously.
- Do not withdraw objects immersed in a cryogenic liquid without using tongs.
- Avoid the path of boil-off gases.
- Keep ignition sources away when handling cryogenic liquids especially liquid oxygen. Combustible materials (including the user) may become oxygen-enriched or saturated through exposure and, in the presence of an ignition source, will ignite rapidly and burn fiercely.

- Never plug containers holding cryogenic liquid; cover them when not in use to prevent an accumulation of moisture and ice.

5. Storage, Transportation and Spill Issues

a) Storage

Store cryogenics in appropriately labeled and insulated containers (Dewar flasks are commonly used) which minimize the loss due to boil-off. Containers of cryogenics must never be closed so that they cannot vent. Moisture, caustic cleansers, chemicals or other substances which might cause corrosion should be removed at once. Wash containers with plain water or mild detergent solution and then wipe dry. Cryogenics should not be stored in non-ventilated areas such as cold rooms.

b) Cryo-Biological Storage

Cryo-biological storage containers are specifically designed and constructed to withstand the extreme temperature variances involved in handling liquid nitrogen. These special containers should be filled slowly to avoid the expansion stress that occurs as a result of the rapid cooling. Too much stress can damage the container. Cryo-biological storage containers are designed to function with little or no internal pressure. Nitrogen continually evaporates. The use of any tight-fitting stopper or plug that prevents the adequate venting of gas builds up pressure that could severely damage or even burst the container. Even icing or accumulated frost can interfere with proper venting and containers should be checked for such obstructions. To assure safe operations, only the original neck tube core or approved accessories for closing the neck tube should be used.

c) Transportation

Transport of cryogenics within buildings:

Containers should be transferred in handcarts or other devices designed for moving cryogenic liquid vessels. They should not be carried up the stairs due to the risk of tripping and spilling. They also should not be carried by someone up the elevator. If the elevator were to suffer a breakdown, the cryogenic could displace the oxygen in the elevator leading to consequences potentially including death. If cryogenics must be transported by elevator, take adequate precautions to prevent possible injury. Send cryogenics in elevators without any passengers and ensure that no passengers get on the elevator while the cryogenic is being transported. The exception would be for quantities of 1L or less, as that quantity would not be enough to cause asphyxiation in even a small elevator.

Transport of cryogenics between buildings / campuses:

Closed trucks or vans are not recommended for transporting cryo-biological storage containers; ventilation is required to prevent gas from accumulating. In addition, containers should be secured in an upright position to prevent spillage and they should be protected from heavy jolting or colliding with one another.

Certain compressed/liquefied gas cylinders or containers are subjected to the *Transportation of Dangerous Goods Regulations (TDGR)*; be aware of the rules/exemptions before shipping any cryogenic materials by road transportation. If unsure, please contact EHS (ehs@concordia.ca) for information.

Shipments on dry ice:
The shipment of any goods on dry ice (solid carbon dioxide) requires special means of containment and is controlled under the *Transportation of Dangerous Goods Regulations (TDGR)*; be aware of the rules / exemptions before shipping any material on dry ice. If unsure, please contact EHS (ehs@concordia.ca) for information.

d) Spills

Most of cryogenics will turn into gases as soon as they are released free. In the event of a small spill (≤1L), evacuation may not be necessary if the area is well-ventilated. However, if you begin to feel dizzy or lightheaded, shut off the cryogenic liquid, close the tank, and leave the area temporarily to get some fresh air. Let the area ventilate well before going back in.

In the event of a **large cryogenic spill**, follow these guidelines:

1. Advise and warn co-workers.
2. Evacuate the area immediately.
3. Restrict the access to the area.
4. Notify Security at **3717** or **514 848-3717**, providing them with the following information:
    a. Location of the spill
    b. Name of hazardous material
    c. Quantity involved
    d. Related health risks and precautions to be taken
5. Evacuation of the surrounding rooms / labs and its occupants may be necessary depending on the volume of cryogenic liquid spilled and its relative hazard.

6. Emergency Procedures

a) Skin Contact

1. Rewarm the affected area as quickly as possible by immersing it in **warm** (about 42°C) (but not hot) water. Severe burning pain, swelling, and color change may occur during warming. Warming is complete when the skin is soft and sensation returns.
2. Do not rub the affected tissues.
3. Do not apply heat lamps or hot water and do not break blisters.
4. Cover the affected area with a sterile covering and seek assistance as you would for burns.
5. Call Security at **3717** for emergency medical assistance.

b) Eye Contact

1. Immediately wash the affected eye with large amounts of water (approximately 15 minutes).
2. Do not allow the victim to rub or keep eyes closed.
3. Call Security at **3717** for emergency medical assistance.

c) Inhalation

1. Immediately move the victim to fresh air.
2. If breathing is difficult, administer oxygen.
3. Call Security at **3717** and ask for medical assistance.

d) Ingestion

Not likely a route of entry as liquefied gases / cryogenics readily evaporate.

e) Hypothermia

People appearing to be 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.

In all cases of exposures, a copy of the Safety Data Sheet (SDS) must be brought to the emergency room as the treating physician might be unaware of the treatment measures for cryogenics. All cryogenics incidents must be reported to your Supervisor and to Environmental Health & Safety. An Injury / Near-miss Report must be filled for any incident involving cryogenics spill or exposure.

If you have any concerns about the use of cryogenics at Concordia University, please contact EHS at **ehs@concordia.ca**.

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References:

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- *Safety Data Sheet; AirGas Liquefied Nitrogen(N2); 2013*
- *Safety Data Sheet; Air Liquide Oxygen, refrigerated liquid; 2013*
- *Safety Data Sheet; Chemwatch Helium liquid; 2013*
- *Safety Data Sheet; Chemwatch Argon, refrigerated liquid; 2013*
- *Material Safety Data Sheet; Chemwatch Carbon dioxide, solid; 2014*
- *STANDARD OPERATING PROCEDURE: Cryogenic Liquids, Harvard EHSHLC, 10/23/2008*
- *Répertoire Toxicologique CNESST www.csst.qc.ca*