# CRYOGENIC LIQUIDS AND THE SCIENTIFIC GLASSBLOWER

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## INTRODUCTION

It is common practice for scientific glassblowers to construct glassware that will be used by researchers for cryogenic experiments. 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). All cryogenic liquids are gases at normal temperatures and pressures. 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. An awareness of the potential hazards of cryogen use will allow the glassblower to construct apparatus that will reduce the risks of working with these super-cold liquids.

There are three 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.

## HEALTH HAZARDS

There are four groups of health hazards associated with cryogenic liquids: extreme cold, asphyxiation, overpressurization, and toxicity.

- Extreme Cold Hazard: Cryogenic liquids and their associated cold vapors 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. (See Figure A - Treatment of Frostbite)

- 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. Large volumes of nitrogen gas are evolved from small volumes of liquid nitrogen and this can easily replace normal air in poorly ventilated areas leading to the danger of asphyxiation. It should be noted that oxygen normally constitutes 21% of air. Atmospheres containing less than 10% oxygen can result in brain damage and death (the gasping reflex is triggered by excess carbon dioxide and not by shortage of oxygen), levels of 18% or less are dangerous and entry into regions with levels less than 20% is not recommended.

- Overpressurization Hazard: Small amounts of liquid can evaporate into very large volumes of gas. For example, one liter of liquid nitrogen vaporizes to 695 liters of nitrogen gas when warmed to room temperature. Closed vessels containing cryogens will explode violently when allowed to warm. A standard wall 10mm glass tubing has an allowable internal pressure rating of 14 atmospheres (about 200 psi). (See Table B - Maximum Allowable Internal Pressure) Small amounts of liquid oxygen in a sealed glass tube can easily produce pressures in excess of 1000 psi when the liquid warms to the gas phase.

- Toxic Hazard**:** 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 material safety data sheet for information about the toxic hazards of a particular cryogen. 1

## CRYOGEN PROPERTIES

Table C (Properties of Common Cryogens) compares properties of some of the most common cryogenic liquids. A common use of liquid nitrogen is as a refrigerant for traps incorporated in vacuum lines. Extreme care must be employed when using liquid nitrogen as a cold trap coolant. Systems including liquid nitrogen traps must never be opened to the atmosphere until the trap is removed from the coolant. Oxygen has a higher boiling point (-183 °C) than nitrogen (-196 °C), and will condense out of the atmosphere and collect in a liquid-nitrogen cooled vessel open to the air. Additionally, liquid oxygen forms highly explosive mixtures with many organic materials.

Argon is a gas commonly employed as an "inert atmosphere" for chemical reactions, Schlenk apparatus, distillations, and other laboratory operations. Argon is unusual because its boiling and freezing points are close, at -186 and -189°C, respectively. The solid state of argon has a very low vapor pressure and may survive exposure to high vacuum for a considerable period of time. Use of liquid nitrogen as a coolant on vacuum systems containing argon maybe hazardous. When the coolant is removed from either a trap or a product sample containing argon, large volumes of gaseous argon will be evolved over a 3°C change in temperature as warming occurs. If you suspect liquid oxygen or argon has condensed in a cold trap, use the following procedure to safely vent the trap: 2

- Continue to cool with liquid nitrogen until the trap has been vented to atmosphere.
- Immediately shield the trap (with an explosion shield, closed hood window, etc.).
- Vent the cold trap to atmosphere. Turn off vacuum pumps.
- If possible, with the trap remaining in liquid nitrogen, lower the trap outer tube. Once removed from the system, the outer tube containing the liquefied oxygen or argon can be removed from the liquid nitrogen dewar. Allow the tube to warm to room temperature. (See note below *).

- If the outer trap tube cannot be lowered, with the trap remaining in the liquid nitrogen dewar, allow the trap (vented to the atmosphere) to slowly warm to room temperature. Post a sign indicating the danger.

(* Standard taper joints are not recommended for cold trap joints. The large taper joints have a tendency to stick and become difficult to remove quickly in an emergency. Glass o-ring joints can be disassembled much quicker in this situation).

## PERSONAL EXPERIENCES

Throughout our careers as scientific glassblowers, we have witnessed several incidents involving cryogens that have caused injury to personnel. By sharing these experiences, it is our hope that we will all have a greater understanding and respect for cryogenic liquids.

- Incident 1: A facility equipped with a large outdoor liquid nitrogen storage tank had the actual delivery piping located in an adjacent room inside the building. The small room was equipped with fresh air ventilation and floor level exhaust ducts to remove nitrogen gas from the room. A chemist transported a large 160-liter liquid nitrogen storage vessel into the room and began filling the tank. Since these tanks can take 30-60 minutes to fill, he returned to his lab to check on an experiment. Sometime (much) later he returned to the fill area to see that the tank had overfilled and liquid nitrogen was spilling out into the room. He entered the room to close the fill valve and within seconds fell to the floor unconscious. A second chemist, who happened by, saw the unconscious victim, recognized seriousness the situation, and was able to pull the victim to safety in the hallway.

  Hazard: Asphyxiation. The air in this confined space was displaced by the spilling liquid nitrogen and had reduced oxygen amounts to dangerous levels. Normal air contains 21% oxygen. Oxygen concentrations below 18% by volume can cause dizziness, rapid heart rate, nausea, vomiting disorientation, mental confusion, loss of consciousness, and death. There is no warning. Oxygen has no odor, color or means of determining concentration without direct measurement.

  Remedy: The liquid nitrogen fill room was fitted with increased ventilation/exhaust equipment, an oxygen level monitor with alarm was installed, and a timer was added to the fill piping that required an attendant restart the fill process every five minutes. Both chemists recovered fully from this incident, but no one should have entered the room under these circumstances.

  Additionally, if dry ice or a dewar containing cryogenic fluids must be transported via an elevator, it should not be accompanied by personnel. Ideally, these materials should be transferred alone. In a typical elevator car with poor air mixing, evaporation of as little as one pound of dry ice can create a breathing impairment.

- Incident 2: A local chemist was required to purify and ship metal samples (europium and cesium) to a company on the US East Coast. The samples were to be shipped in evacuated glass ampoules with glass wool plugs in each end to aid in shipping. The materials are quite reactive in air so the chemist prepared the ampoules in a glove box and poured liquid argon into each ampoule. The intention was to purge the air from the glass wool, metal sample, and glass ampoule. The argon filled ampoules were placed in a dewar of liquid nitrogen for transportation to the glass shop for evacuation and seal off. Liquid argon was added several times in transit to continue the argon purge. Once in the glass shop, the ampoules were warmed above room temperature, evacuated for 30 minutes each, and flame sealed. About one minute after sealing, the chemist picked up one of the ampoules and it violently exploded in his hand. His safety glasses were broken (his eyes were not damaged) but he received multiple cuts to his hands and face. One glass fragment sliced completely through his cheek from just below his eye to the top of his lower jaw. He was transported to a local emergency room for treatment.

Hazard: Overpressurization. This incident involved a double jeopardy. 1) The liquid nitrogen was condensing liquid oxygen inside the open ampoule on the trip across town and, 2) the addition of liquid argon into the ampoule was actually being frozen solid by the liquid nitrogen. Even though the ampoules were warmed while being evacuated, (which would pump off the liquid oxygen rather quickly), the frozen argon was trapped within the glass wool. The solid argon has a very low vapor pressure and resists vacuum pumping for long periods of time. As the temperature of the ampoule slowly increased - so did the internal pressure and the explosion occurred.

Remedy: This is likely the best example of "how not to" prepare samples for shipping. Never immerse open containers in liquid nitrogen. The container will fill with liquid oxygen. Never use argon in a liquid nitrogen cooled vessel. The liquid nitrogen will freeze the argon into a solid and create the potential for explosion when warmed.

- Incident 3: A chemist requested small ampoules (3mm OD glass tubes) sealed at atmospheric pressure with 2ml of chloroform inside. The ampoules were filled and placed into a dewar of liquid nitrogen to lower the vapor pressure of the chloroform during flame sealing. The ampoules were sealed and allowed to warm to room temperature. Each ampoule exploded violently upon warming. There were no injuries in this incident.

  Hazard: Overpressurization. Placing the tubes in liquid nitrogen while open to the atmosphere condensed a large amount of liquid oxygen inside the ampoule.

  Remedy: Because of the danger associated with condensing liquid oxygen, NEVER use liquid nitrogen as a low temperature bath when the container is open to the atmosphere. Instead, use one of the following low-temperature baths (see Table D - Low Temperature Baths). This will enable you to lower the vapor pressure of the solvent for flame sealing without condensing liquid oxygen into the ampoule.

- Incident 4: A chemist visited the glass shop to report that his glass vacuum system appeared to be leaking and not pumping to normal operating pressure. Once in the lab, it was determined that several glass stopcocks were severely leaking due to channeling stopcock grease. The system, which had a liquid nitrogen cold trap, had been pumped all night in this condition. Inspection of the cold trap revealed a large amount of liquid condensed in the trap.

  Hazard: Overpressurization of the glass vacuum system caused by liquid oxygen condensed in the cold trap. Additionally, there was the possibility of organic solvents frozen in the trap which could react violently in the oxygen enriched atmosphere. It appeared there was 6-700ml of liquid collected in the trap. If you detect material in the cold trap in liquid form, assume it to be liquid oxygen and take appropriate action.

Remedy: A safety shield was placed between personnel and the cold trap. The liquid nitrogen dewar remained in place around the cold trap. The cold trap was vented to the atmosphere and the vacuum pumps turned off. With the liquid nitrogen dewar in place around the cold trap, the trap bottom was removed from the system. The dewar of liquid nitrogen and the liquid oxygen filled cold trap bottom were transferred to a chemical fume hood. The dewar and its' contents were left in the hood to warm slowly. A sign was posted on the hood to warn others of the situation. No one was injured in this incident but the potential for disaster was extreme.

## CONCLUSION

As we look back over our careers as scientific glassblowers, most of the dangerous situations we have encountered in the workplace have involved working with cryogenic liquids. These incidents occurred early in our careers when years of experience and knowledge about cryogenic liquids were limited. Some of these lessons were learned the hard way. It is our hope that sharing these experiences with fellow members of the American Scientific Glassblowers Society will help reduce injuries. Take the time to share this information with co-workers and colleagues. When a new graduate student orders a vacuum system from your facility -- take a few minutes to instruct him or her in the potential dangers of working with cryogenics. Tell them what to watch for. You may save a life.

The A.S.G.S. Safety and Hazards Committee

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## FIGURE A

### Frost Bite – What is the difference between frost bite and cryogenic liquid bite?

Frostbite is a scary concept. When we think of frostbite, images of mountain climbers come to mind. It is important to think through the process of frostbite. True frostbite due to the long-term exposure to extreme cold is particularly damaging. In these cases the freezing time was relatively slow.

In extreme frostbite the water in individual cells begins to freeze, beginning with those cells most distal from the central trunk of the body. The freezing process is essentially a migrating front.

Because it freezes slowly the ice crystals that form grow slowly, and they grow LARGE! As the crystals become large they typical outgrow the cell walls themselves. This rupturing of the cell wall is usually non-reparable by the body, or medical personnel. The flesh is so severely damaged that amputation is necessary.

In the case of freezing via contact with Cryogenic Fluids (liquid nitrogen or argon) the water in the cells freezes extremely fast. This process is essentially a quenching process, and thus cells walls do not rupture. The trick to prevent permanent damage in the case of a liquid nitrogen or liquid argon skin freeze is too NOT rub the area. Allow the frozen area to warm up by processes that will not cause intercellular damage.

## TABLE B

## MAXIMUM ALLOWABLE INTERNAL PRESSURE (MAIP)
## (IN ATMOSPHERES)

**Wall Thickness (mm)**

| **Outer Diameter (mm)** | **0.2** | **0.4** | **0.6** | **0.8** | **1** | **1.5** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **0.6** | 45 | | | | | | | | | | | | | | |
| **0.8** | 34 | | | | | | | | | | | | | | |
| **1** | 27 | 54 | | | | | | | | | | | | | |
| **2** | 14 | 27 | 41 | 54 | | | | | | | | | | | |
| **3** | 9 | 18 | 27 | 36 | 45 | | | | | | | | | | |
| **4** | 7 | 14 | 20 | 27 | 34 | 51 | | | | | | | | | |
| **5** | 5 | 11 | 16 | 22 | 27 | 41 | 54 | | | | | | | | |
| **6** | 5 | 9 | 14 | 18 | 23 | 34 | 45 | | | | | | | | |
| **7** | 4 | 8 | 12 | 16 | 19 | 29 | 39 | 58 | | | | | | | |
| **8** | 3 | 7 | 10 | 14 | 17 | 26 | 34 | 51 | | | | | | | |
| **9** | 3 | 6 | 9 | 12 | 15 | 23 | 30 | 45 | 60 | | | | | | |
| **10** | 3 | 5 | 8 | 11 | 14 | 20 | 27 | 41 | 54 | | | | | | |
| **11** | 2 | 5 | 7 | 10 | 12 | 19 | 25 | 37 | 49 | 62 | | | | | |
| **12** | 2 | 5 | 7 | 9 | 11 | 17 | 23 | 34 | 45 | 57 | | | | | |
| **13** | 2 | 4 | 6 | 8 | 10 | 16 | 21 | 31 | 42 | 52 | 63 | | | | |
| **14** | 2 | 4 | 6 | 8 | 10 | 15 | 19 | 29 | 39 | 49 | 58 | | | | |
| **15** | 2 | 4 | 5 | 7 | 9 | 14 | 18 | 27 | 36 | 45 | 54 | 63 | | | |
| **16** | 2 | 3 | 5 | 7 | 9 | 13 | 17 | 26 | 34 | 43 | 51 | 60 | | | |
| **17** | 2 | 3 | 5 | 6 | 8 | 12 | 16 | 24 | 32 | 40 | 48 | 56 | 64 | | |
| **18** | 2 | 3 | 5 | 6 | 8 | 11 | 15 | 23 | 30 | 38 | 45 | 53 | 60 | | |
| **19** | 1 | 3 | 4 | 6 | 7 | 11 | 14 | 21 | 29 | 36 | 43 | 50 | 57 | 64 | |
| **20** | 1 | 3 | 4 | 5 | 7 | 10 | 14 | 20 | 27 | 34 | 41 | 48 | 54 | 61 | |
| **22** | 1 | 2 | 4 | 5 | 6 | 9 | 12 | 19 | 25 | 31 | 37 | 43 | 49 | 56 | 62 |
| **25** | 1 | 2 | 3 | 4 | 5 | 8 | 11 | 16 | 22 | 27 | 33 | 38 | 44 | 49 | 54 |

**Undamaged Pyrex™Tubing**
**Temperature = 25°C**
**Ambient Pressure = 1 ATM**
**1 ATM = 14.7 PSI**

**Example**
**10mm OD Pyrex™ tube**
**1mm wall thickness**
**MAIP = 14 atmospheres**
**14 atm X 14.7 psi = 205.8 psi**

The following formula will yield the maximum allowable internal pressure in a piece of undamaged PYREX™ tubing.

$$P = 2000\ X\ \frac{W}{OD}\text{ , PSI}$$

P = Allowable Internal Pressure
W = Minimum wall thickness, mm.
OD = Maximum outside diameter, mm.

## TABLE C

### PROPERTIES OF COMMON CRYOGENS

| Gas | Temperature in Liquid Phase °C | Boiling Point °K | Volume of Expansion Liquid to Gas | Flammable | Toxic | Odor |
|---|---|---|---|---|---|---|
| Helium-3 | -269.9 | 3.2 | 757 to 1 | No | No(a) | No |
| Helium-4 | -268.9 | 4.2 | 757 to 1 | No | No(a) | No |
| Hydrogen | -252.7 | 20.4 | 851 to 1 | Yes | No(a) | No |
| Neon | -245.9 | 27.2 | 1438 to 1 | No | No(a) | No |
| Nitrogen | -195.8 | 77.3 | 696 to 1 | No | No(a) | No |
| Carbon Monoxide | -192.0 | 81.1 | ________ | Yes | Yes | No |
| Fluorine | -187.0 | 86.0 | 888 to 1 | No | Yes | Sharp |
| Argon | 185.7 | 87.4 | 847 to 1 | No | No(a) | No |
| Oxygen | -183.0 | 90.1 | 860 to 1 | No | No(a) | No |
| Methane | -161.4 | 111.7 | 578 to 1 | Yes | No(a) | No |
| Krypton | -151.8 | 121.3 | 700 to 1 | No | No(a) | No |
| Xenon | -109.1 | 164.0 | 573 to 1 | No | No(a) | No |
| Nitrous oxide | -89.5 | 183.6 | 666 to 1 | No | No(a) | Sweet |
| Acetylene | -84.0 | 189.1 | ________ | Yes | Yes | Garlic |
| Carbon dioxide | -78.5 (b) | 194.6 | 553 to 1 | No | Yes(a) | Pungent |

(a) Nontoxic, but can act as an asphyxiate by displacing air needed to support life.
(b) Sublimes
(c) °K = 273.16 °C; 459.69°F

## TABLE D

**LOW TEMPERATURE BATHS**

| SYSTEM | °C |
|---|---|
| Ethylene glycol/$CO_2$ | -15 |
| o-Xylene/$N_2$ | -29 |
| Acetonitrile/$CO_2$ | -42 |
| Chloroform/$CO_2$ | -61 |
| Chloroform/$N_2$ | -63 |
| Ethanol/$CO_2$ | -72 |
| Acetone/$CO_2$ | -77 |
| Methanol/$N_2$ | -98 |

Two types of systems are shown in this table. One involves pouring liquid nitrogen (boiling point -196°C) into a solvent by stirring until slush is formed. The temperature may be maintained by periodically adding nitrogen to maintain the slush. The second system involves addition of small lumps of dry ice to the solvent until a slight excess of dry ice coated with frozen solvent remains. Again, temperatures may be maintained by periodically adding more dry ice.

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