



Christian Gianese

Main hazards associated with the use of low temperatures

- ✓ **Low temperatures**
- ✓ **Evaporation**
- ✓ **Pressure**
- ✓ **Physico-chemical**
- ✓ **Transport of fluids**

Hazards associated with low temperatures

➤ **Cryogenic liquid**

- ✓ Splashes of liquid
- ✓ Immersed in liquid (very rare!)

➤ **Jet of cold gaz**

- ✓ Rupture of transfer pipe, valve not closing, relief valve
- ...

➤ **Contact with cold surfaces**

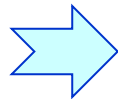
- ✓ Removal of a transfer pipe, a cryostat, ...

*These phenomena are conditioned by
heat exchanges*

a. Heat exchanges by radiation

$$Q = \varepsilon \cdot S \cdot \sigma \cdot (T_2^4 - T_1^4)$$

Cold
area
 $T = 4\text{K} !$



No radiation risk !

$$Q = 1 \times S \times 5,67 \cdot 10^{-8} \times (300^4 - 4^4) = 46 \text{ mW/cm}^2$$

b. Heat exchanges by conduction

1 – By no insulated parts

Contact of the skin with the cold part

* Transfers limited by the epidermis

$K(\text{skin}) \sim 1,5 \text{ W/cm at } 300 \text{ and } 4\text{K}$

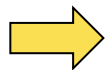
thermal conductivity, k , is the property of a material's ability to conduct heat

Fourier's Law

$$Q = \frac{S}{L} \int_{T_1}^{T_2} k(T) dT$$



Heat exchange very fast



Tissues are damaged very quickly

2- with cryogenic liquids

Heat exchanges are difficult in the liquid



When you immerse a "warm body" in a liquid, there is formation of a gas film over the surface (Calefaction)



Calefaction: Protective Phenomenon ($\sim 1\text{sec}$)

« *You can put your hand in liquid nitrogen ...* »

▪ Splashes

Usually occur during the transfer of fluids

- ❑ Not very dangerous to the skin (caustification)



Danger on clothing
Stiffening of clothes



Clothing becomes like a "sponge", it holds the liquid

▪ Jets of liquid



• **Very dangerous !**

The energy available in a jet is very important

Energy available in a stream of nitrogen : 308 J/g from 77K to 300K

■ Cryo burns

a. Contact of the skin



The severity of "burns" and frostbite with liquid nitrogen is more characterized by the depth of the lesions rather than their extent.

The more rapid the cooling down is:

- the more important the cell destruction is
- the deeper is the wound

The fastest the warming is:

- The more cells are surviving

▪ Cryo burns

b. Contact ocular



Very brief exposure to liquid nitrogen or cold vapors **can damage the eye tissue** and cause frostbite, sometimes leading to **irreversible damage** or blindness



Prévention

• Personal protective equipment



- » Wear insulated gloves without holes
- » Wear goggles or face shield
- » Beware of shoes !




• General Rules

- » Be alert
- » Beware of security parts (relief valves = risk of jets)
- » Be careful during transfers

Note that there is no glove suitable for immersion in liquid nitrogen !

Treatment of cryo burns

- Remove clothing
(Risk of progression of the burn if the garment is cold)
 - Heat the "burned" areas with warm water over a large area (20 min)
 - Protect cryo burns with a sterile cloth
-  Depending on the severity, bring the injured person to a hospital

Hazards with evaporation of fluids

- **Asphyxiation**
- **Over pressurization of equipment**

•Asphyxiation



Vaporization of cryogenic liquid releases very large volumes of gas
(700 times the liquid volume for nitrogen)



*Poorly ventilated room: reduction in oxygen content
(underground, tunnel, etc.)*

The human body is very sensitive to oxygen concentration

Normal level of oxygen in the air: 21%

Ancient Greek:

Zôé: Life

A-zote: prevents life !! (Antoine Lavoisier)

▪ Symptoms based on the rate of oxygen

21 %	Normal	
18 %	Alarm threshold	
14 %	Lower faculties (unconscious)	} potentially fatal
11 %	Fainting	
6 %	Immediate loss of consciousness	

Evaluation of oxygen in a room

1. Normal evaporation of a liquid nitrogen tank (evaporation 6% / day)

$$C_{O_2} = 21 \cdot \left(1 - \frac{1,7 \cdot 10^{-3} \cdot V_{LN_2}}{V \cdot n}\right)$$

C_{O_2} Residual oxygen concentration (% volume)
 V room volume in m³
 n rate of air change in room volume per hour
 V_{LN_2} volume of liquid nitrogen stored in L

Exemple: room 6m x 6m x 2.8m = 100 m³

V_{LN_2} stored = 200 L

$n = 0.5$ (no special ventilation)

$C_{O_2} = 20.8 \%$ No danger

2. Tank Falling down

$$C_{O_2} = 21 \cdot \left(1 - \frac{0,682 \cdot v_{LN_2}}{V}\right)$$

C_{O_2} Residual oxygen concentration (% volume)

V room volume in m³

v_{LN_2} volume of liquid nitrogen fell from the container Litres

Exemple: room 6m x 6m x 2.8m = 100 m³

V_{LN_2} fell = 20 L

$C_{O_2} = 18 \%$



Danger

Prevention

- ☐ Put exhaust and relief valves to the outside
- ☐ Check periodically cryogenic equipments
- ☐ Training personnel on the dangers, risks and preventive measures to take
- ☐ Use appropriate trolleys to transport the containers of cryogenic liquid

In confined spaces, underground, basement, cellar:

- Collective protection
 - Oxygen sensors (to be tested regularly)
- Personal protection
 - Portable oxygen meter
 - Alarm if $O_2 < 18\%$
 - Buzzer
 - Light signal

Equipment under pressure

Gaz Storage

1. Bottle of compressed gas

- Gas supply, purge gas, welding,
 - stored at high pressure (200 bar, more)



Stored energy is huge!

Stored energy is huge!

Brode formula:

$$W = \frac{(P_1 - P_2) \cdot V}{\frac{C_p}{C_v} - 1}$$

V m³
P Pa
W Joules

Calculation for a volume of helium

50 liters at 200 bar



$$W = 1,5 \cdot 10^6 \text{ joules}$$

equivalent to 0.3 kg of TNT!



2. Rupture of compressed gas unit

- Pressure wave

- Significant effort on the major surfaces
 - Walls, windows (danger of projections)
 - Ruptured eardrums (pressure difference very fast, no accommodation)

- Missiles

- Term used by firefighters to describe a piece projecting off at high speed

Prevention



Secure HP cylinders

Chek security features



Cryogenic liquefied gas

Pressure problem: Depending on the rate of evaporation



Significant risk if rupture of the thermal insulation

- Deterioration of the vacuum insulation
- Contact heat
- ...

Another problem is significant release of energy in the cryogenic liquid
ex: « quench » of superconducting coil

If there is a rupture of the material: identical result to a pressurized bottle at ambient temperature but with the added risk of cryogenic burns

Prevention

- Respect the design of equipment
 - safety factor
 - regulation, control
 - safety equipment (relief valves, etc)
 - use good materials

Materials



Generally when the temperature decreases

Improving the strength of materials

- Breaking
- yield strength
- Young Modulus



But, for some materials

Phenomenon of embrittlement

- Decrease of residual elongation
- Decrease of resilience (shock resistance)

Importance of knowing the materials that become brittle in cold

Thermal expansion

Important phenomena in cryogenic assemblies

1. Thermal expansion of metals

Most of the contraction between room temperature and liquid nitrogen temperature

(Little expansion from 4.2 K to 77 K)

2. Thermal expansion of "plastics" (amorphous)

- Up to 10 times that of metals
- There may be expansion and contraction

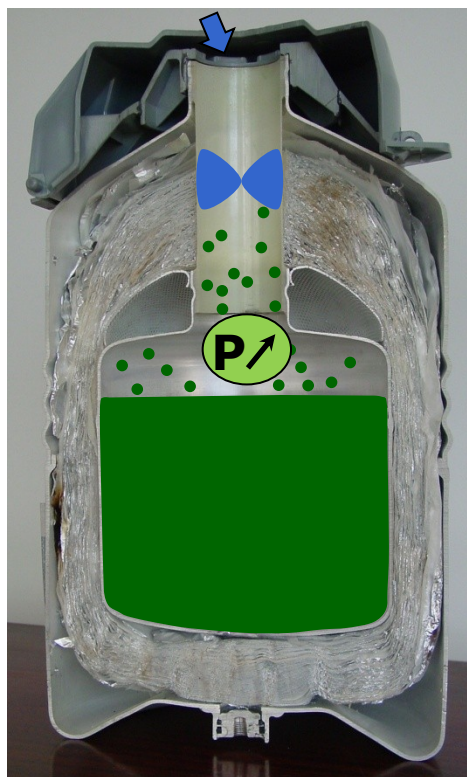
Humidity

Open vessel

Water vapor condenses in the neck of the vessel and can clog it

Danger if pressure rise !

Humidity



Plug !

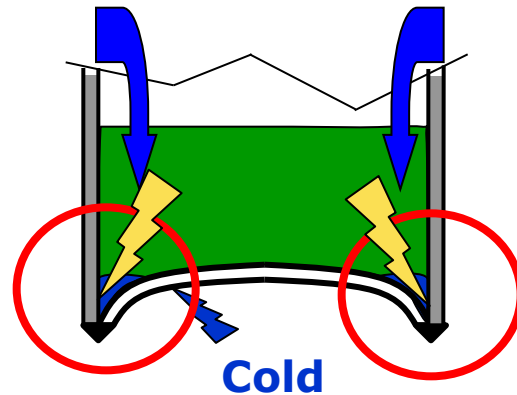


❑ Solutions

- Plug
- Maintain an overpressure in the vessel
- Relief valves

- With Helium dewar: double neck

Accumulation of water

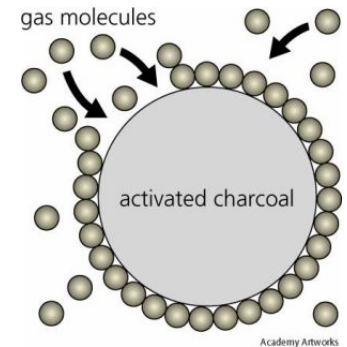


**Ice = Expansion
= Break**

Adsorbents (charcoal, silicagel, ...)

Process in which molecules of gas, adhere in an extremely thin layer to surfaces of solid bodies with which they are in contact.

*The degree of adsorption depends on temperature, pressure, and the surface area. The forces binding the adsorbate to the adsorbent (solid surface) may be physical or chemical;
chemical adsorption is specific, and is used to separate mixtures*



Adsorbents (charcoal, silicagel, ...)

Frequently used in cryogenics to improve the vacuum insulation

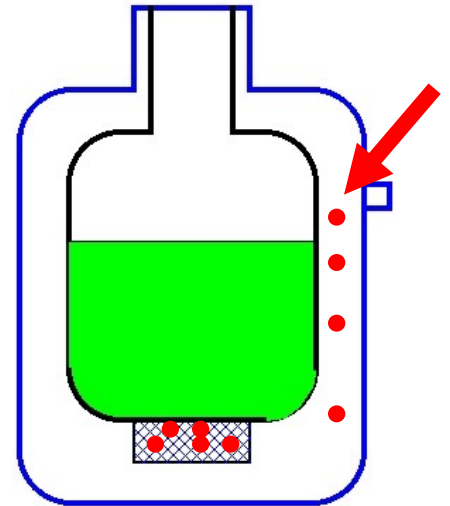
In contact with cold surfaces, they compensate the degassing and micro leaks

If leaks: progressive trapping.



The stored quantities can be significant

Trapped volume = some 100 cm³/gram of coal



Adsorbents

When heating

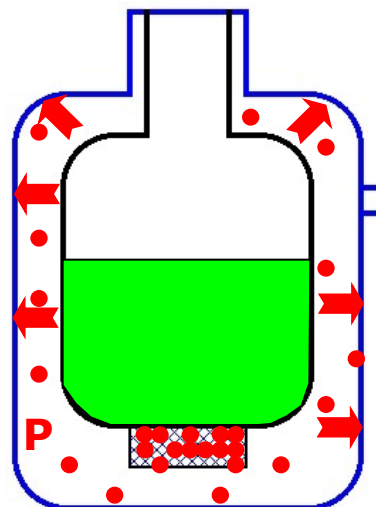
Phenomenon of desorption of trapped molecules



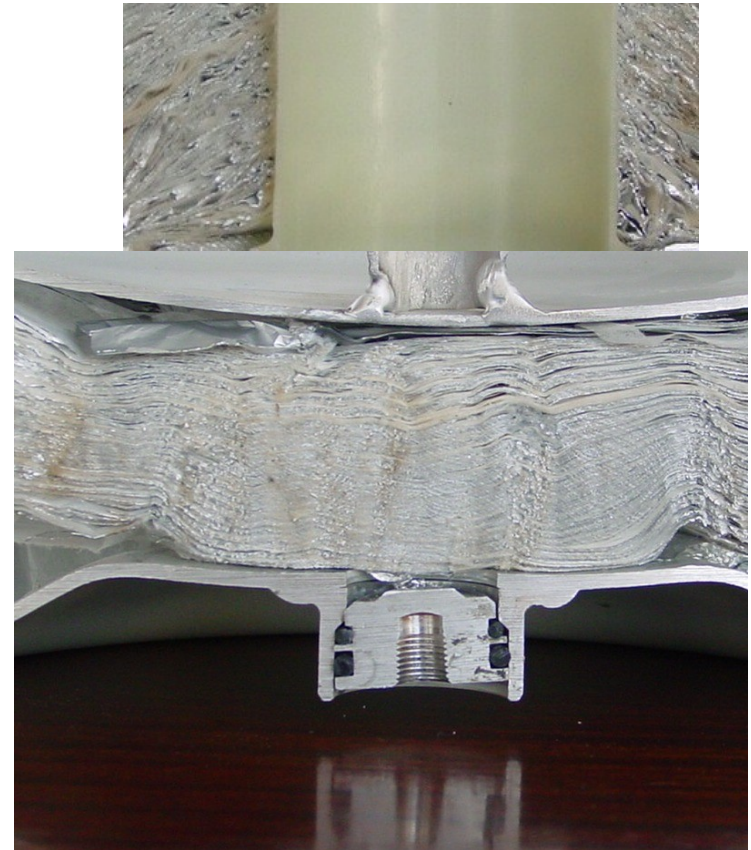
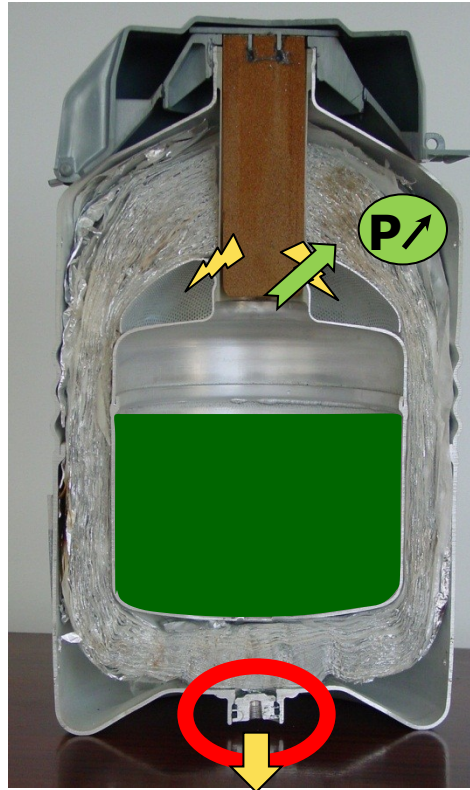
Risk of over pressure

Security features

- Rupture disk
- Dump valve / Relief valve
- etc ...



Shock



Explosion of a liquid nitrogen dewar



Chemical Hazards

1. Toxic gases

❑ Cryogenic gases are mostly neutral

- Nitrogen, helium, argon, ...
(Safe, except asphyxia)

❑ Some used cryogenic gas in liquefied form can be dangerous

- Ozone (O_3) ...
- Carbon monoxide(CO)
- Hydrogen



- Precautions: toximeters (same as oxygen)

1. Ozone

- ❑ Occurs naturally in the atmosphere
 - 0.005 to 0.05 ppm in air
 - Produced by UV radiation or electrical discharge
- ❑ Highly reactive gas
 - Could explode in liquid state
 - Very powerful oxidizing agent

Ozone



Result of toxicity with humans

- Severe lung injury (9 ppm)
- Decreased visual acuity
- Renal and neurological (1-2 ppm)

Carbon monoxide

Use:

- Chemical synthesis
- Nickel refining
- Industrial fuel

Metastable compound

Colorless, odorless

Is formed when combustion with oxygen deficiency

Carbon monoxide



Human toxicity: legal limit ~50 ppm

☐ Mechanism:

Affinity with the hemoglobin

When 50% of the hemoglobin is saturated with CO: fatal

Hydrogen



Very dangerous

- Extremely flammable
- Extensive area of explosion
- Odorless, colorless
- Very volatile
- Asphyxiant at high concentrations

Hydrogen



Precautions

- Room ventilated to the outside
- Explosion-proof equipment specific H2
- Prohibition of flame

Storage

- Grounded (static electricity)
- Isolated area
- Access to regulated areas
- Staff trained in specific hazards H2

Oxygen

□ Properties

at 21%, it sustains life



Beyond 23%

- Risk of explosions

O₂ is heavier than air (1.105)

Oxygen



Very dangerous

- Greasy substances ignite spontaneously: oils, greases, paper
- Wood, asphalt impregnated with O₂, adsorbent, ... can become explosive

Oxygen



Precautions

- No contact between O₂ liquid and inflammable bodies
- Room ventilated to the outside
- Detector with threshold of sensitivity > 23%
- Do not smoke

- Regulate the storage areas



Use Specific equipment (O₂)

- Regulators, gauges, etc. without grease
- Reversed thread (not confused)

Storage and transport

Liquid storage vessel

- Subject to traditional regulation of pressure vessels (depending on country)
- Particular requirements for liquefied gas containers



Never close the vents

Relief Valves required before any closure equipments (valve, plug, ...)

Gas storage

Subject to traditional regulation of pressure storage (depending on country)

- Re-tests decennial and quinquennial (in France)
- Safety valves

Access is strictly regulated

General information on transport

The transport of dangerous goods, all around the world, has strict regulations, recommendations from the UN.

For Europe is the "European Agreement concerning the International Carriage of Dangerous Goods by Road" governing the safe transport of dangerous goods.

It did not become a law, each contracting country ensures control over its territory under its own law.

General information on transport

Orange panel with:

NU code

1977: liquid nitrogen
1963: liquid helium
1966: liquid hydrogen
...



Hazard Identification Number

- 2...: gas
- 22...: refrigerated gas
 - inert
 - 3: flammable
 - 5: combustion
 - 6: toxic
 - 8: corrosive

Hazard symbol:



Transport of cryogenics vessel

- Vessel in the standard transport rules
- Check the relief valves
- Open the special relief valve of transport (DP \sim 20 mbar)
- Firmly secure in upright position

- Sealed wall between the cab and the load
- Driver trained in cryogenic risk

Merci

