Cryogens in the Department of Physics

*Arguably, liquefied helium and nitrogen pose the greatest threat to life in this Department. This threat exists not just for those who conduct experiments, but all who use the premises. Therefore **everyone** should understand the nature of the risks and what to do if things appear to be going wrong. At the very least, everyone should be familiar with the instructions on this web page: http://www.phy.cam.ac.uk/internal_resources/hands/emergencies/asphyxiation*

This code gives advice on the control of risk from liquefied gases (principally helium and nitrogen), solid CO_2 and the piped supply of nitrogen that comes from the main tanks.

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1. Introduction

The Department of Physics uses significant quantities of liquid nitrogen and liquid helium and also has a network of pipes throughout many of the buildings delivering gas from the tanks. This represents an effectively unlimited supply of asphyxiant gas. The following key risks are therefore present in the department:

- Asphyxiation - due to the displacement of air,
- Damage to the insulation on electric cables - which could lead to electrocution,
- Condensation of water onto nearby electrical equipment,
- Condensation of liquid oxygen onto the pipework, etc, when drawing off liquid nitrogen or helium - leading to a fire risk,
- Blockage of outlets from cryogenic containers, leading to a risk of explosion,
- Burns - due to touching cold metal, getting clothing soaked with cryogen, or direct contact with the liquid.

(this is not an exhaustive list!)

2. Effects Of Liquid Gases

2.1 Asphyxiation

You will find tables listing the symptoms and signs of reduced oxygen on the human body. Please treat these with extreme caution as they are misleading. The onset of asphyxiation can be rapid, and there are likely to be no obvious warning signs to the victim. There are no physical symptoms of distress, and the function of the brain is seriously impaired in an oxygen deficient atmosphere, without the person's knowledge. It can take as little as two breaths in an oxygen deficient atmosphere to cause unconsciousness, and death will occur within minutes. Below around 10%, death or brain damage may be inevitable, even if the casualty is rescued and resuscitation is attempted.

The atmosphere normally contains approximately 21% oxygen by volume. Atmospheres containing less than 18% oxygen are potentially dangerous, and entry into atmospheres containing less than 20% oxygen is not recommended.

Accident records show that, for almost every person who is overcome and dies in an atmosphere that does not support life, an additional person dies, unsuccessfully attempting a rescue.

2.2 Changes in material properties

We have all seen people smashing rubber hose, etc, when doing demonstrations with liquid nitrogen. In polymers this is primarily due to the fact that cryogenic liquids take the material well below its glass transition temperature, into a regime where it is brittle. It recovers if it is warmed up - but it may break if it is disturbed while cold, or if it contains residual stresses. The most tragic demonstration of this change in material properties was in the loss of the Challenger in 1986.

Floor tiles crack, and may come away from the floor. These can cause trip hazards, and in any case are unsightly. Carpet tiles appear to be just as vulnerable as lino. Pneumatic tyres on vehicles that are exposed to liquid nitrogen may explode.

Carbon steels (i.e. not stainless) are body centred cubic, and also become dramatically more brittle at low temperatures. They are not suitable for low temperature service.

The drains cannot cope with liquid nitrogen - the materials can be damaged - expensively. If the damage is not immediately apparent, think what might happen if someone puts a chemical down the drain - where might the leaked material go to?

2.3 Condensation of water

Most of the time, the air is well laden with water vapour and, in consequence, wherever you are using cryogens, you will have water vapour condensing out and often forming significant ice burdens on pipes, etc. This can give rise to a risk of electrocution, or items being broken under the weight of the ice. Water may drip onto precious equipment.

2.4 Condensation of liquid oxygen

Since oxygen has a higher boiling point than nitrogen, it can condense into liquid nitrogen. Fortunately it is a light blue colour, so if it has condensed in a significant quantity into an open Dewar of nitrogen it is obvious. Be aware that liquid oxygen is a serious fire hazard, and pure oxygen can cause organic materials to ignite spontaneously or explode.

What is less well known is that the liquid that forms and runs off a nitrogen delivery tube from a Dewar when you are discharging nitrogen is also very rich in oxygen. Hence smoking is prohibited at nitrogen transfer points. Liquid that is allowed to dribble onto clothing can take a very long time to disperse, and the individual is in considerable danger while their clothing is rich in oxygen - do not get the liquid on your clothing, and do not go out and smoke immediately after conducting a nitrogen transfer.

2.5 Blockage of outlets

Liquid helium can readily cool air below its freezing point, and solid air is quite 'sticky'. It can block up bits of your apparatus (the author speaks from experience!). If the apparatus becomes blocked, then it is possible that an explosion may result, because the helium will evaporate before the blockage clears itself.

Blockages can form above liquid nitrogen as well, if ice forms in sufficient quantity. Dewars must not be left outside when it is raining.

The standard solution to the problem of requiring an outlet that will not block is the Bunsen valve - a piece of rubber tube with a slit in it, cheap and very effective for nitrogen Dewars. Helium Dewars must be connected to the laboratory helium gas return line.

2.6 Burns, frostbite

Liquefied gases, particularly when soaked into clothing, can produce burns that are similar to heat burns. Unprotected skin may also stick to un-insulated items and flesh may be torn on removal.

More prolonged contact can cause the flesh to freeze. While frozen it will appear yellow and waxy, and will probably not hurt, but when it thaws, it is likely to give rise to intense pain. Such burns require immediate medical attention.

Persistent, superficial contact with liquid nitrogen can also give rise to chilblains - itchy, red, irritated patches of skin on the hands.

Breathing in the cold gas can trigger asthmatic attacks in susceptible individuals.

3. Legal Requirements

There is no legislation specific to cryogens. However, there are three basic legislative requirements:

- to ensure so far as is reasonably practicable, that people are not exposed to risks to their health and safety
- to undertake a risk assessment to define how this will be achieved
- to be aware that, under certain circumstances, a room or area may become especially dangerous to life through lack of oxygen, to detect when this may happen, and take steps to prevent people from entering the danger area.

4. Accident Case Histories

One research facility 'lost' a number of the old narrow-necked Dewars (the tiltable ones that were mounted on wheeled trolleys). It turned out that each weekend they were taken out of doors. Some still had small quantities of nitrogen in them. It is surmised that the necks of the Dewars were being blocked by ice, and at some time over the weekend they were exploding!

In 1999 there was a fatal accident in a research establishment, where a technician was filling Dewars. He had around ten years experience. The boil-off during the filling process was sufficient to reduce the oxygen concentration in his room below that which would support life. His colleagues, who attempted to rescue him, nearly suffered the same fate and one was very lucky to survive.

In a workplace where they had both piped nitrogen and piped air, someone accidentally connected some breathing apparatus to the nitrogen line. A workman donned the breathing apparatus and immediately collapsed. He could not be resuscitated and died.

A workman put his head into the opening of a tank in which his colleagues had been working. He took a couple of breaths of the air inside the tank, and died, even though he only had his head in the opening.

These incidents should be borne in mind when planning your contingency arrangements.

5. Risk Assessment: Step 1 - Assessing The Hazards

5.1 Asphyxiation

Record the identity of the cryogen, what you are using it for, and the maximum quantity of liquid gas that you have in a single container in the room (whether inside the apparatus or inside the Dewar).

Calculate the volume of the room. Then calculate the minimum oxygen content, based on the assumption that the cryogen from a single container escapes and simply displaces air from the room. Nitrogen expands to 680 times the volume of liquid, and helium expands to 740 times the volume of the liquid.

If the cryogen is piped into the room, then record the maximum quantity that could be accidentally dumped in the room, and calculate the oxygen concentration in the same way.

There is a network of pipes bringing nitrogen gas from the liquid nitrogen tanks into many of the labs. Since the tanks contain many thousands of litres of liquid, this means that the supply is effectively unlimited. Thus, it is important to identify whether your room has such a supply and how it is being used.

There is a useful spreadsheet calculator that will do the calculations
http://www.phy.cam.ac.uk/internal_resources/hands/hazards/Cryogens2/Oxygencalculator/view
Simply select the correct tab for the cryogenic
gas you have, and enter in the data in the yellow boxes. If the result of your calculation is 18% or less, there may be a problem. For piped nitrogen, use the tab marked 'gas release'.

The spreadsheet model is limited. It assumes that the inert gas has leaked into the room, displacing air in equal amount, and that the inert gas has mixed with the air that is left. In reality, the atmosphere close to the item that is leaking is probably depleted in oxygen to a far greater extent than the above calculation would indicate. One could also argue that cold nitrogen will tend to accumulate near the floor, and helium above the head. However, if the gas is released rapidly, there will be turbulence and mixing.

Now that you have done the calculation for the room, please repeat it for the corridors where you leave the large Dewars, and the spaces through which cryogenic liquids are piped.

Consider now what will happen - how will the air be replenished? How quickly will it be replenished? Is the position the same at night, or at the weekends?

All of this can be recorded on a form that has been designed for the purpose. See appendix A.

5.2 Other properties

These are usually fairly obvious, and can be seen from the layout of the equipment - in other words, there is a risk if the electrical cables are on the floor close to the nitrogen top-up tube, etc.

Have a good look at the way in which jobs are done, to spot the other sources of hazard that crop up.

5.3 Solid carbon dioxide

Carbon dioxide is toxic. While you might also suppose that it is an asphyxiant, high levels of carbon dioxide in the atmosphere will be fatal long before it reaches a value where it threatens the oxygen supply to your brain.

6. Assessing The Risk

6.1 Asphyxiation

The calculations done so far give you a simplistic account of the intrinsic hazard. You now have to work out the risk that the dangerous event might happen. To do this you need to work out how the cryogen could be released in that quantity. You need to consider such events as:

- Fracture of a pipeline
- A pressure relief valve sticking open
- The loss of vacuum in an insulating jacket
- Knocking over the helium or nitrogen Dewar
- A magnet quenching
- Opening the wrong tap on the nitrogen Dewar and leaving it open, etc.

Many of these have already happened at some time. Many of them pose a real danger to life.

Some of these will be sudden and spectacular, and if someone is present when they occur, they will perhaps react to them. However, the event may happen at night, or it may happen to a person who is injured or knocked unconscious. What will happen then? What if a Security guard is the first to find the problem?

While helium is lighter than air, and nitrogen is marginally denser, do not assume that they will be released in neat layers. If there is turbulence, they will mix, and once mixed, they will not separate again (you can buy cylinders of 5% hydrogen in nitrogen - they will be uniformly mixed indefinitely!)

In general, you only need to worry about a single failure mode - e.g. if you have two magnets in a room, only one may quench. Clearly if there are likely to be two failures that will be linked by cause and effect you need to consider them both.

If a particular sequence of events has happened once, then it becomes a known cause, and must be taken into account and planned against. For example, if it is known that someone has overfilled and over-pressurised a system in the past, whether it was due to utter carelessness on their part or not, it is something that you have to guard against in the future. (quote from a judge 'you have a duty of care not just to the careful and diligent worker, but also the lazy and indolent').

Examples where the piped nitrogen supply may be released include one of the connections coming apart, or if a glove in a glove box is lost or punctured.

6.2 Other hazards

Nothing beats a good inspection to spot how the cryogen can give rise to problems. Write down your findings, and plan to reduce the risk so far as is reasonably practicable. Listen to the folk-lore of the area - what has gone wrong in the past? You cannot dismiss a risk because someone did something idiotic - you must expect this kind of behaviour from newcomers and those who are becoming over confident, or wish to cut corners.

6.3 Carbon dioxide

The gas calculator has a page for carbon dioxide. The data can be handled in the same way as the nitrogen or helium data. However, note the warnings about the exposure limits for this gas and the levels at which fatality can occur.

7. Reducing The Risk

7.1 Asphyxiation

Now that you have the basic information about your system, you need to make some decisions. The hierarchy you should adopt is as follows:

- Remove the problem altogether, which may be achieved by having less cryogen in the space (e.g., not leaving the Dewar in the room)
- Ensure that cryogen from your apparatus is vented to a space that is large enough to accept it without threatening the oxygen level.
- If you have a piped nitrogen supply, ensure that all the connections are of a high integrity (welded, brazed or swagelock).
- Ensure the ventilation level is adequate to disperse the gas (but check on the status of the ventilation system at night or at weekends).
- Reduce the probability of accidental release by ensuring the stability of Dewars, maintaining the floor in good condition, training your personnel, using labels and diagrams, etc, to remind the forgetful.
- Impose procedural control - such as prohibiting the transport of cryogens in a lift along with personnel, prohibiting the transfer of cryogens at night, unless at least two people are present.

The second step in the hierarchy is dealing with a risk that you cannot engineer out. e.g. Where you believe that it would be advisable, place oxygen monitors in the area, or give out personal oxygen monitors. You may choose this on the basis of, say

- the sheer quantity of cryogen involved,
- a high risk activity such as cryogen transfer,
- the possibility of an unforeseen leak,
- the possibility of a person being forgetful, or
- the possibility of multiple failure.

You may, for instance, decide to interlock the oxygen monitor to an emergency ventilation system.

> If you invest in oxygen monitors, do not forget to put in place a programme of maintenance and inspection. They are no use if they are not calibrated, or their batteries are flat!

If your hazard is carbon dioxide, remember that an oxygen monitor will only tell you of the danger AFTER the atmosphere has reached a fatal level. Invest instead in a carbon dioxide monitor!

7.2 Damage to insulation and other materials, condensation of water

This needs good experimental design. Ensure that cables are not placed where they are likely to be affected by liquid nitrogen spills. This may demand some ingenuity for the leads to the apparatus, and you may have to site the leads off the ground.

Condensation problems can be dealt with in the same way. Make sure that ice and condensation cannot lead to water mixing with electricity.

Train people not to pour liquid nitrogen down the drains, or over the floor tiles (it's good fun, but the floor does often get irrevocably damaged). Ensure that when you design widgets for cryogenic service, you choose suitable materials.

7.3 Condensation of liquid oxygen

Train people to avoid getting oxygen-enriched liquid on their clothing. Ensure there is a 'no-smoking' policy at places where cryogens are transferred.

7.4 Blockages of outlets to apparatus

Your apparatus is likely to have several over-pressure prevention measures such as safety valves or Bunsen valves for atmospheric pressure release, which will have been put in at the design stage.

Management of this risk is largely by training - people need to become familiar with the system that they are using, and this takes time. Don't let a newcomer cool down apparatus on their own until you have done it with them several times, ensured that they understand the layout of the system (a diagram and written instructions would be helpful!) and know the danger points in the procedure, and what to do if something goes wrong.

7.5 Burns

These usually arise when pouring nitrogen or transferring helium. Ensure that you train people about the risk of getting frozen to the pipework, etc.

Make sure the gloves you issue are the right type - loose fitting cryogenic gloves. It is no good giving people gloves that soak up nitrogen! Eye protection is essential when transferring cryogenic liquids into open buckets.

Ensure that people wear the gloves and goggles - it's important.

8. Contingency Planning

Even when you have done your best to devise a safe system of work, something can go wrong. It is important to ensure that everyone knows what to do.

What if?

- You come across a vapour cloud?
- You hear an oxygen meter alarming?
- A Dewar falls over?
- Someone collapses in a laboratory?
- The piped nitrogen supply is leaking into the room?
- Liquid nitrogen is spilling uncontrollably from a Dewar?
- Someone trips and breaks their ankle while carrying a liquid nitrogen container?

Some pointers (not exhaustive):

- It is probable that a visible vapour cloud is significantly depleted in oxygen. Personnel should be instructed never to enter a vapour cloud.
- people should know where the portable oxygen monitors are - they may need them.

If there are pipelines that have an effectively unlimited source of cryogen or asphyxiant gas (e.g. nitrogen delivery, helium return) the layout of the system needs to be demonstrated to people, along with some sort of warning system to alert people to the failure, and many people need to know how to isolate the problem - NOT JUST THE OWNER OF THE EQUIPMENT!

Remember that the first person to find your equipment in a state of failure may be a Security Guard. A notice indicating where the nearest cutoff valve (accessible without going into the room!) is

> Don't assume that an oxygen meter will automatically save people's lives. You still need to think through an action plan and train people.
>
> Otherwise, they may simply turn the meters off, to stop the horrible noise that they are making!
>
> They may also take a deep breath and enter the room in the mistaken belief that this is the right thing to do.

located would be most helpful.

Evacuation procedures need to be thought through - both from the point of view of getting people out safely, but also keeping them out until it is safe.

Personnel need to know how to get a first aider quickly and efficiently.

People need to be trained to cope with a collapsed casualty, so that they do not become the second casualty.

A sheet of emergency and first aid instructions is Appendix B. A notice template for rooms that have an oxygen monitor is in Appendix C.

Appendix A: Form for the Assessment of Cryogenic Apparatus

Filled in by ……………………………………… Date ……………………………..

Initial assessment

Room Number/ Space being analysed	
Note: the calculation below can be done using a spreadsheet at http://www.phy.cam.ac.uk/internal_resources/hands/hazards/Cryogens2/Oxygencalculator/view	
Maximum quantity of cryogen in the room at one time (include Dewars that are brought in for filling purposes)	
Volume of gas if it evaporates (x 680 for nitrogen, x 740 for helium)	
Convert to cubic metres (1000 litres in one cubic metre), V_1	
Volume of the room, V	
Fraction of oxygen left if all the cryogen escapes (simple model: $0.21\ (1 - V_1/V)$)	
Is this less than 0.18?	*If yes, go to the next section. If no, go to the last section.*

Planning to reduce likelihood of having an oxygen deficient atmosphere.

How could the cryogen escape? (e.g. slow boil off, quench, knocking the Dewar over) The measures you need will depend on the way in which the cryogen is released.	
Can it be prevented from happening? (e.g. ensuring that the vent is to the outside, or that a Dewar is not left in the room)	
If the ventilation were improved, could this solve the problem? (check about the arrangements at night).	
Are the preventative measures dependent on a human being remembering something? (If so, they are inherently less sound).	
Action Plan	

Contingency planning

Is it still reasonably foreseeable that the cryogen could escape into the room, and render the atmosphere less than 18% oxygen?	
Are there any procedural measures that can reduce the likelihood?	
Will it be obvious that the cryogen has escaped? (e.g. will there be a warning sound so that I do not enter a room with little oxygen in it)	
Do you have an emergency plan to handle this situation?	
Have the personnel in the area been fully informed? Have they practised it?	
Have arrangements been made to maintain and test any monitoring equipment, or equipment needed for rescue purposes?	

If there is still a perceived need for rescue with the use of breathing apparatus, then please see the Safety Officer, since this needs a permit-to-work system (i.e., rescuers need to be trained, ready and standing by whenever the dangerous operation is being carried out).

Skills and procedures

Does everyone know how to use the Dewars correctly? (e.g. the right taps, the right way to use a transfer tube, the right clothing to wear, etc.)	
Does everyone know what to do if they make a mistake? (e.g. knock over a Dewar, break off a tap, etc)	
Does everyone know what to do if they hear an oxygen alarm?	
Does everyone know what to do if they find a vapour cloud?	
Does everyone know what to do if they see a person collapsed on the floor in a room?	
Does everyone wear the correct personal protective clothing when transferring cryogens? (gloves and specs)	

The list of people, to whom the above questions regarding procedures and emergency

procedures relates, is kept ……………………………………………

Jane Blunt, December 2010

Appendix B: Emergency Procedures and First Aid

Burns:

In severe cases summon medical attention (by ambulance) immediately. Flush affected areas of the skin with copious quantities of tepid water (around 40° C, but NOT MORE THAN 45° C) to reduce freezing of the tissue. However, a large burn when warmed up will cause the casualty much distress and the casualty will require powerful pain relief. If there is likely to be a delay in transport to the hospital, then allow the burn to warm up more slowly.

Loosen any clothing that may restrict the circulation of the blood. Do not apply heat to the affected parts, but keep the casualty warm. Cryogenic burns will swell and are very prone to infection. Protect the burned area from infection or further injury.

The casualty department may not have treated a liquid nitrogen burn before. Take the MSDS detailing the medical treatment required with the casualty to the hospital.

Large Spills of Liquid Nitrogen:

Do not enter the 'fog' cause by large liquid nitrogen spills, the oxygen concentration in the fog may be well below that of normal air.

Large spills out of doors should be dispersed with water, to increase the rate of vaporisation. If a vehicle has been involved, do not move it until the tyres are warm again.

For a large spill inside a building the area must be evacuated. It may not be appropriate to use the fire bell to do this, since people may enter the danger area on their way out. Move away from the danger area and call on the assistance of colleagues, using oxygen meters to protect yourselves, then call for help from the Safety Officer, or at night initially from the Security Staff. Ensure that they know the danger of asphyxiation and are wearing their oxygen meters.

Asphyxiation:

Once successfully rescued, treat as for any unconscious casualty – give artificial ventilation.

Note – attempts to rescue someone who has been overcome, without the correct equipment and training, are almost certain to end with additional casualties. DON'T DO IT. To be effective in any way you must minimise the risk to yourself.

Appendix C: Notice for rooms where there is oxygen monitoring

Do you hear an alarm sounding in this room?

It indicates low levels of OXYGEN

Do not enter the room

Priority is to check for a casualty

Can you see into the room?

YES

- If you can see a casualty, call lists A, B, C.
- If there is no casualty, get someone to assist you, preferably from list C.
- Find another oxygen meter and check that it is working.
- Cautiously open the door and put the meter through the gap.
- If the meter sounds, close the door and call someone from list C.
- If it does not sound, enter the room and silence the alarm. Leave a report on what has happened.

NO

- Get someone to assist you – either someone nearby or someone from list C.
- Knock loudly on the door. If no response then find another oxygen monitor and check that it is working.
- Cautiously open the door and put meter through the gap (if door is locked, call someone from list C).
- If meter sounds, close door and call lists A, B, C.
- If meter does not sound then enter the room and silence alarm and leave a report on what has happened.

List A: **Fire Brigade, 1-999,** to rescue a casualty from an oxygen-deficient atmosphere. You MUST inform them of the oxygen deficiency.
Ambulance, 1-999, if the atmosphere is oxygen deficient they must wait for the Fire Brigade to rescue the casualty.
If out of normal working hours, then also call **Security, on 37499,** to help with access.

List B: **Jane Blunt, 37499, or 078 1760 2858**

List C: **(People responsible for the room)**