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1.0 HAZARDS AND REGULATIONS

Simple Asphyxiants

Gases which have no toxic action but cannot support respiration, which is to say non-toxic gases excluding oxygen, are known as *simple asphyxiants* or just *asphyxiants*.¹ Mixing any asphyxiant gas with air dilutes the overall oxygen concentration and may result in an oxygen deficiency hazard (ODH). The commonest simple asphyxiants likely to be used in sufficient quantity to make ODH a potential concern are nitrogen and helium. Other examples of simple asphyxiant gases include nitrous oxide, argon, hydrogen, gaseous hydrocarbons (methane, ethane, etc), carbon tetrafluoride, sulfur hexafluoride, and refrigerant gases such as hydrofluorcarbons (HFCs). Carbon dioxide has a definite toxic action and is not classified as a simple asphyxiant; it is covered in a section below.

Oxygen Concentration and Partial Pressure

The normal atmosphere contains 20.95 % oxygen by volume (Table 1); this concentration is virtually constant from sea level to the stratosphere. Normal atmospheric pressure at sea level (closely approximating to the altitude of USC) will support a column of mercury 760 mm high, this being denoted 760 mmHg or equivalently 760 torr.

In a mixture of gases, each gas exerts a *partial pressure* independent of the others, and adding all the partial pressures of all the components of the mixture gives the total pressure. It is the partial pressure of oxygen in air which directly mediates the physiological effects of oxygen on the human body. Partial pressure and concentration have the following simple relationship:

Atmospheric pressure × (vol. % oxygen concentration / 100) = oxygen partial pressure

Using the above relationship, the normal sea level atmosphere of 760 mmHg pressure and 20.95 vol. % oxygen is easily seen to have an oxygen partial pressure of 159 mmHg.

Atmospheric pressure decreases with increasing altitude in an approximately exponential manner. The importance of oxygen partial pressure is that it encompasses the effect on the human body of both changing altitude and changing oxygen concentration. Thus, reducing the oxygen concentration breathed at sea level has the same effects on the body as breathing the normal atmosphere at higher altitudes.

¹ The Cal/OSHA Hazard Communication regulation (<u>8 CCR §5194</u>) gives the following definition of a Simple Asphyxiant: "A substance or mixture that displaces oxygen in the ambient atmosphere, and can thus cause oxygen deprivation in those who are exposed,

A partial pressure of oxygen down to 132 torr is not considered to cause any adverse physiological effects in healthy humans; this partial pressure is equivalent to breathing normal air at 5000 feet altitude, or air at sea level containing 17.2 vol. % oxygen.²

Component	Concentration / vol. %	Concentration / vol. ppm	Partial pressure at sea level mmHg (torr)
Nitrogen	78.09	780,900	593
Oxygen	20.95	209,500	159
Argon	0.934	9,340	7
Carbon dioxide	0.0335	335*	0.3
Trace gases (He, Ne,	0.0027	27.1	0.02
CH4, Kr, H2, N2O, Xe, O3)			
Total	100	1,000,000	760
* Over 400 now, d	lue to human fossil fuel co	ombustion.	

Table 1. Components of the standard dry atmosphere

(after https://www.taylorfrancis.com/books/e/9780203740347, Table 3.1, p67)

Effects of Oxygen Deficiency

Oxygen deficiency is an insidious hazard. Human bodies do NOT contain adequate systems for measuring oxygen levels in blood, rather, respiration is regulated via feedback mechanisms based on sensing of blood carbon dioxide concentration. In an oxygen deficient atmosphere, CO₂ is breathed out as normal so there is zero sensation of suffocation or breathing difficulty. If the asphyxiant gas in the atmosphere has no taste or smell, which is the case for the commonest simple asphyxiants, an individual entering a dangerous atmosphere will not have any immediate indications that there is a hazard present.

The heart and especially the brain are the human organs most sensitive to oxygen deficiency. After entering a moderately oxygen deficient atmosphere, an individual will begin experiencing increasing loss of mental faculties (see Table 2). This state impedes proper decision making and commonly prevents the affected individual from recognizing that anything is wrong. Pilots who undergo hypoxic training in hypobaric chambers often describe the sensation of oxygen deficiency as being similar to alcohol inebriation, with a relaxed feeling and no sensation of impending danger. If an affected individual is not able to extricate themselves from a low oxygen atmosphere (which is a common occurrence in industrial accidents), they may become increasingly dizzy and unaware of their surroundings before slipping into unconsciousness. Permanent cardiac or brain damage or death may result.

Unconsciousness occurs <u>extremely rapidly</u> on entering a severely oxygen deficient atmosphere (see Table 2, below). The lungs equilibrate oxygen between the blood and the atmosphere, meaning that oxygen already in the blood will be breathed out if the oxygen concentration in the surrounding atmosphere is low enough.

² Reference: Documentation of the Threshold Limit Values and Biological Exposure Indices, ACGIH, 2015. Simple Asphyxiants and Carbon Dioxide Program: Hazards, Risk Assessment, and Mitigation Hazards, Risk Assessment, Assess

A typical individual can hold their breath for about 40 seconds (considerably longer if they are a trained swimmer) without any reduction in consciousness as the blood contains a significant oxygen reserve. However, unconsciousness occurs suddenly after taking only one or two breaths in a minimal-oxygen atmosphere, since under these conditions the blood is stripped of its oxygen reserves on passing through the lungs, and the deoxygenated blood passes straight to the brain. Death follows quickly.

Table 2. Physiological effects of breathing	g low oxygen atmospheres.
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Vol % O ₂ in atmosphere at sea level 20.95	Partial pressure O ₂ / torr*	Equivalent to breathing normal 20.95% O ₂ air at altitude / ft 0	Effects None
17.2	131	5000	None in healthy adults.
16.6	126	6000	Possible impairment of night vision. FAA: "At night, because vision is particularly sensitive to diminished oxygen, a prudent rule is to use supplemental oxygen when flying above 6,000 feet". (Ref. d)
16.0	121	7000	This is the oxygen concentration at which adverse effects first become noticeable in healthy humans. Increased breathing and blood flow, reduced coordination, impaired mental faculties.
15.4	117	8000	Possible altitude sickness in individuals who are not acclimatized (headache, nausea, vomiting).
14.4	109.5	10,000	FAA: "For best protection, you are encouraged to use supplemental oxygen above 10,000 feet". (Ref. d)
13.7	104	11,000	Fatigue, poor coordination, impaired judgement.
13.3	101	12,000	FAA considers 12,000 feet as the maximum altitude at which hypoxia is not a serious risk; "Any aviator who flies above 12,000 feet in an unpressurized aircraft without supplemental oxygen is a potential hypoxia case." (Ref. c, below) General aviation supplemental oxygen requirements begin at 12,500 feet.
12.3	93.5	14,000	FAA regulated maximum altitude for flying an unpressurized aircraft without supplemental oxygen. Maximum time



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Vol % O ₂ in atmosphere at sea level	Partial pressure O ₂ / torr*	Equivalent to breathing normal 20.95% O ₂ air at altitude / ft	Effects
			limit of 30 mins is applied, after which supplemental oxygen shall be used or the aircraft shall descend to below 12,500 ft. (General aviation regulations, 14 CFR § 91.211).
12.2	93	14,000	Impaired respiration, very poor judgment and coordination, tunnel vision. Nausea and vomiting. Permanent heart damage is possible. (ACGIH, ref. a, below.)
10.5	79.5	18,000	"Time of useful consciousness" of 20-30 mins; less if physically active, fatigued, or unhealthy. Time of useful consciousness rapidly reduces at higher altitudes / lower oxygen concentrations.
<10	<76		Nausea, vomiting, lethargic movements or loss of all movement, unconsciousness, death.
<6	<46		Shortness of breath, rapid unconsciousness, convulsions, cardiac arrest, spasmodic breathing, death in minutes.
<4	<30		Sudden unconsciousness after one or two breaths, death rapidly follows.
Exposure Ind. McManus, 19	ices, ACGIH, 2015; b) 1 999, CRC Press, availat	Table 3.12, p91, S ple online	reshold Limit Values and Biological afety and Health in Confined Spaces, Neil 10347; c) FAA Aviation Physiology
			pchures/media/hypoxia.pdf

According to the National Institute for Occupational Safety and Health (NIOSH), "At oxygen concentrations below 16% at sea level, decreased mental effectiveness, visual acuity, and muscular coordination occur. At oxygen concentrations below 10%, loss of consciousness may occur, and below 6% oxygen, death will result. Often only mild subjective changes are noted by individuals exposed to low concentrations of oxygen, and collapse can occur without warning." (https://www.cdc.gov/niosh/docs/2005-100/default.html)

According to <u>Aviation Physiology</u>, published by the Federal Aviation Administration, "One factor that tends to make hypoxia so dangerous is its insidious onset.

Any aviator who flies above 12,000 feet in an unpressurized aircraft without supplemental oxygen is a potential hypoxia case." 12,000 feet altitude corresponds with a partial pressure of oxygen of 101 mmHg, which is equivalent to breathing a 13.3% oxygen atmosphere at sea level. FAA regulations permit flying in an unpressurized cabin without supplemental oxygen for a maximum of 30 minutes at altitudes between 12,500 and 14,000 feet; above 14,000 feet supplemental oxygen is required for the flight crew.³ 14,000 feet corresponds to an oxygen partial pressure of 93.5 mmHg, equivalent to breathing a 12.3% oxygen atmosphere at sea level. At an altitude of 18,000 feet the oxygen partial pressure is 79.5 mmHg, equivalent to a sea level atmosphere containing 10.5% oxygen. At this altitude, a healthy individual might expect a "time of useful consciousness" or "effective performance time" of 20-30 minutes, after which they will not have the mental acuity to take proper decisions (*Aviation Physiology*). This time may be significantly reduced by physical activity, poor health, sudden exposure to the low oxygen environment, and other factors.

The relationship between the concentration of a simple asphyxiant gas mixed with air and the resulting oxygen concentration of the mixture is given in Table 3, below.

Concentra simple as gas in air / vol. %		Resulting concentration of oxygen / vol. %	Liters of liquid N ₂ evaporated into a 10x15x12 ft. room to give indicated oxygen concentration*	Hazard (at sea level atmospheric pressure)
0	0	20.95	0.0	
1	10,000	20.74	0.7	None
5	50,000	19.90	3.7	None
6.92	69,200	19.50**	5.1	
10	100,000	18.86	7.3	Unlikely to significantly affect healthy
15	150,000	17.81	11	humans; however, such a large
20	200,000	16.76	15	concentration of asphyxiant gas in the
23.6	236,000	16.01	17	atmosphere would be extremely concerning and indicate a serious failure of safety controls.
25	250,000	15.71	18	Impaired metal and physical abilities.
30	300,000	14.67	22	Recognition of the danger and taking of
35	350,000	13.62	26	appropriate action may not be possible.
40	400,000	12.57	29	Serious impairment making self-rescue difficult or impossible. Permanent health damage is possible.
50	500,000	10.48	37	Total incapacitation followed by collapse.

Table 3. Relationship between concentration of simple asphyxiant in air and the resulting oxygen concentration and hazard.

³ Passengers are required to have supplemental oxygen above 15,000 feet in an unpressurized aircraft. Note: The regulations referred to are for "general aviation"; different regulations apply to commercial air transport.

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Concentration of simple asphyxiant gas in air / vol. % / vol. ppm		t Resulting Evaporated into concentration of oxygen / vol. % Liters of liquid for evaporated into 10x15x12 ft. room to give indicated oxyge concentration*		Hazard (at sea level atmospheric pressure)
				Permanent brain damage or death are likely outcomes, depending on exposure time.
60	600,000	8.38	44	
70	700,000	6.29	51	
80	800,000	4.19	59	Immediate collapse rapidly followed by
90	900,000	2.095	66	death
100	1,000,00 0	0	73	

* Simple worst-case calculation based on liquid nitrogen boiling to gas with displacement of an equal volume of air from the room, followed by complete mixing of the nitrogen with the remaining air.

** 19.5% oxygen is the dividing line below which an atmosphere is considered as oxygen deficient.

Note: Cold nitrogen gas is considerably denser than room temperature air. Rapid boiling of liquid nitrogen may result in a stratified atmosphere with a much higher than expected concentration near the ground, or in extreme cases, up to head height.

Oxygen Deficiency Hazards and Standards/Regulations

<u>NIOSH Publication No. 2005-100</u> states: "NIOSH defines an oxygen-deficient atmosphere as any atmosphere containing oxygen at a concentration below 19.5% at sea level." Furthermore, "The minimum requirement of 19.5% oxygen at sea level provides an adequate amount of oxygen for most work assignments and includes a safety factor. The safety factor is needed because oxygen-deficient atmospheres offer little warning of the danger, and the continuous measurement of an oxygen-deficient atmosphere is difficult."

According to the American Conference of Governmental Industrial Hygienists (ACGIH), "The minimum requirement of 19.5% oxygen at sea level (148 torr ρO_2 , dry air) provides an adequate amount of oxygen for most work assignments and incudes a margin of safety."⁴

In California, Cal-OSHA does not allow employers to expose employees to an atmosphere containing less than 19.5% oxygen unless the employees are protected by suitable respirators. This is explicitly laid out in <u>8 CCR §5149</u>, "Oxygen Deficiency", which states "Except in extreme emergency involving imminent peril to life, employees shall not be permitted to work without approved respiratory equipment where the oxygen content of the air is less than 19 1/2 percent by volume (dry basis)." This regulation applies universally across USC.

 ⁴ Documentation of the Threshold Limit Values and Biological Exposure Indices, ACGIH, 2015.

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Note that at USC, no person shall enter an oxygen deficient atmosphere with the exception of suitably trained and equipped members of USC Hazmat and first responders such as LAFD.

Cal-OSHA regulation of "permit-required confined spaces"⁵ (<u>8 CCR §5157</u>) also covers oxygen deficiency hazards: "Oxygen deficient atmosphere means an atmosphere containing less than 19.5 percent oxygen by volume." Furthermore, "Hazardous atmosphere means an atmosphere that may expose employees to the risk of death, incapacitation, impairment of ability to self-rescue (that is, escape unaided from a permit space), injury, or acute illness from one or more of the following causes... Atmospheric oxygen concentration below 19.5 percent..." Normal rooms such as laboratories fall outside the Cal-OSHA definition of permit-required confined spaces,⁵ but places like tanks which admit of human entry and sunken pits containing liquid nitrogen tanks may require a confined space permit. The confined space program is managed by the EH&S Occupational Health division, email injuryprevention@usc.edu for more information.

In USC facilities, any situation where oxygen concentration falls below 19.5% shall be regarded as an unacceptable emergency necessitating evacuation of the area until the atmosphere returns to normal. The area shall not be reoccupied until LAFD or USC Hazmat has deemed the atmosphere to be safe and has given explicit permission for reentry.

Since laboratory work at USC is conducted at a negligible altitude above sea level, the effects of altitude in exacerbating oxygen deficiency hazards need not be considered.

Carbon Dioxide Toxicity and Regulations

Carbon dioxide is not a simple asphyxiant, although it is often mistaken for one. Although a normal component of the human body and completely non-toxic in low concentrations, breathing high enough concentrations in air will cause physiological distress, including respiratory stimulation, headache, dizziness, inability to concentrate, and unconsciousness. These effects occur at CO₂ concentrations in air which are substantial, but not high enough to cause dangerous oxygen deficiency (see Table 4). In extremely high concentration, such as might occur if dry ice (frozen carbon dioxide) is stored in an unventilated space such as a cold room, almost immediate unconsciousness will occur as a result of combined oxygen deficiency and CO₂ toxicity.

Although extreme carbon dioxide concentrations produce an acid sensation in the nose/sinuses, familiar to anyone who drinks carbonated beverages, the presence of a hazardous carbon dioxide concentration in the atmosphere does NOT give adequate warning of the danger.

⁵ Cal/OSHA regulations (<u>8 CCR §5157</u>) give the following definition of a confined space: "Confined space means a space that:

⁽¹⁾ Is large enough and so configured that an employee can bodily enter and perform assigned work; and

⁽²⁾ Has limited or restricted means for entry or exit (for example, tanks, vessels, silos, storage bins, hoppers, vaults, and pits are spaces that may have limited means of entry.); and

⁽³⁾ Is not designed for continuous employee occupancy."

A "permit-required confined space" is a confined space which may entrap an individual, engulf them in a liquid or solid material, contains or has the potential to contain a hazardous atmosphere (including an oxygen deficient atmosphere), or which contains any other recognized serious safety or health hazard.

Effect/Condition	CO ₂ concentration		Time of exposure	Resulting O ₂ concentration	Mass of dry ice evaporated into a
	/ vol. ppm	/ vol. %		/ vol. %	8x8x8.5 ft. room* to give indicated concentration / lb
Normal atmosphere	400	0.04		20.95	0
No or insignificant effects	5,500 – 15,000	0.55- 1.5		20.8-20.6	0.32-0.91
Slight effect, weakly narcotic, reduced hearing acuity, increased blood pressure and pulse	30,000	3		20.3	1.8
Respiratory volume doubled (deeper and faster breathing)	40,000	4		20.1	2.5
Respiratory volume redoubled (deeper and faster breathing)	50,000	5		19.9	3.1
Headache, restlessness, dizziness	75,000	7.5	7-15 min	19.4	4.6
Increase in heart rate and blood pressure, shortness of breath, throbbing headaches, dizziness, vertigo, poor memory, inability to concentrate, photophobia	76,000	7.6		19.4	4.7
Unconsciousness	>100,000	>10	(prolonge d)	<18.9	6.2
Unconsciousness	110,000	11	(<1 min)	18.6	6.8
Unconsciousness	300,000	30	25 s	14.7	18.6

Table 4. Effects of exposure to carbon dioxide in air

Based on Table 3.21, p102, *Safety and Health in Confined Spaces*, Neil McManus, 1999, CRC Press, available online <u>https://www.taylorfrancis.com/books/e/9780203740347</u>

* Size of a small cold room. Simple worst-case calculation based on dry ice evaporating and displacing an equivalent volume of air from the room, followed by the carbon dioxide mixing with the remaining air.

Being a toxic gas rather than a simple asphyxiant, carbon dioxide has legal (Cal-OSHA) exposure limits and NIOSH IDLH value (see Table 5 for values and explanation).

SIMPLE ASPHYXIANTS AND CARBON DIOXIDE PROGRAM: HAZARDS, RISK ASSESSMENT, AND MITIGATION

Table 5. Carbon dioxide exposure limits

Limit	Concentration / ppm	Source	Comments	Mass of dry ice evaporated into a 8x8x8.5 ft. room** to give indicated concentration / lb
Cal- OSHA PEL	5000	Table AC-1	<u>8 CCR §5155</u> : Permissible Exposure Limit (PEL). The maximum permitted 8-hour time-weighted average concentration of an airborne contaminant.	0.29
Cal- OSHA STEL	30,000*	Table AC-1	8 CCR §5155: Short Term Exposure Limit (STEL). A 15-minute time- weighted average exposure which is not to be exceeded at any time during a workday even if the 8-hour time- weighted average is below the PEL.	1.8
NIOSH IDLH	40,000	https://w ww.cdc.go v/niosh/idl h/124389. html	Concentration considered "immediately dangerous to life or health". <u>Definition</u> : <i>Immediately Dangerous to Life or</i> <i>Health (IDLH) condition: A situation</i> <i>that poses a threat of exposure to</i> <i>airborne contaminants when that</i> <i>exposure is likely to cause death or</i> <i>immediate or delayed permanent</i> <i>adverse health effects or prevent</i> <i>escape from such an environment</i>	2.5

* CO₂ does not have a ceiling limit. According to <u>8 CCR §5155 (c)(2)(B)</u>, when a ceiling limit is not specified, the maximum acceptable concentration at any point in time may be taken as the STEL multiplied by 1.5. For CO₂, that would equal 45,000 ppm. Since the NIOSH IDLH value is lower at 40,000 ppm, it seems reasonable to take that value as a ceiling which shall not be exceeded at any time. ** Size of a small cold room.

2.0 LAB SAFETY AND CO₂/SIMPLE ASPHYXIANTS

Hazards Outline

As explained previously, atmospheres containing excessive CO_2 or simple asphyxiants do NOT give any adequate warning of danger. Furthermore, at high enough concentrations of CO_2 /asphyxiant, collapse and death is very rapid. These two factors taken together make for a potent hazard which has claimed <u>numerous lives in industry</u> and academia. In one illustrative case, the contents of a walk-in freezer were kept cold by dry ice while a faulty door was replaced.

The dry ice was not removed after fitting the new door, resulting in a high-CO₂ low-O₂ atmosphere within the freezer. A worker entered the freezer, collapsed, and died (<u>https://www.sciencedirect.com/science/article/pii/S0736467908003284</u>). For the interested reader, a quick internet search will reveal many other cases, and in a significant proportion of them additional casualties resulted from unprotected rescuers entering the hazardous atmosphere and succumbing.

In rooms of typical size, relatively large quantities of asphyxiant gas has to escape into the atmosphere to create a significantly reduced oxygen concentration. However, a localized low oxygen hazard may be created by much smaller quantities of asphyxiant gas in spaces of small volume or where density differences and lack of air currents allow a raised concentration of asphyxiant gas to accumulate. Examples where this might occur include a floor well or unventilated basement room.

Typical nitrogen, argon, or helium high pressure cylinders at USC contain roughly 200-300 cu. ft of gas (measured at atmospheric pressure; refer to the Appendix for more information on cylinder sizes). In normally ventilated labs, a small or even a large leak of gas from a cylinder is not likely to pose any oxygen deficiency hazard. Catastrophic cylinder failure may produce an oxygen deficient atmosphere for a short time, but sudden catastrophic failure is an extremely unlikely event given the rigorous DOT-mandated testing high pressure cylinders are required to periodically undergo. There is more potential for gas leaks to create an oxygen deficient atmosphere in unventilated closets or basement rooms. As a general rule, gas cylinders shall not be stored or used in unventilated basements. Unventilated closets housing gas cylinders are covered in more detail in a following section.

In general, cryogenic liquids (nitrogen, helium, argon) have much greater potential to create oxygen deficiency hazards than gas cylinders. One liter of cryogenic liquid produces approximately 25-30 cu. ft of gas on boiling, representing a volume increase of about 700-840 times (see Tables 9 and 10 in Appendix for exact values for specific cryogens). A 160 L pressurized liquid nitrogen container stores a colossal 3936 cu. ft of nitrogen gas. Cryogens evaporate into the atmosphere slowly but continuously during storage and rapidly during many common operations (e.g. refilling Dewars) or when spilled. As a toxic gas, carbon dioxide is a slightly more potent health hazard on a volume basis than simple asphyxiants. Cylinders of CO₂ contain liquid, either at room temperature and high pressure in strong steel cylinders, or refrigerated liquid at lower pressure in insulated cylinders (see Appendix for full details). As such, carbon dioxide cylinders have a higher capacity than cylinders of "permanent gases" (gases which cannot be liquefied by pressure at room temperature, including He, Ar, N₂); a typical high pressure CO₂ cylinder contains 64 lb gas equivalent to 561 cu. ft. Refrigerated liquid cylinders are much larger, usually 300 lb or more of carbon dioxide.

Dry ice (frozen carbon dioxide) sublimes slowly on storage so must be stored in areas of adequate size and ventilation. On spillage, dry ice evaporates far more slowly than cryogenic liquids, and in general it is used in smaller quantities than liquid nitrogen. Thus, atmospheric hazards from dry ice are low provided it is not taken into unventilated spaces (e.g. basements, cold rooms), small closets, or other enclosed volumes such as passenger vehicles. One pound of dry ice sublimes to 8.76 cu. ft of gas (refer to Appendix for fuller details, including a description of the phase behavior of carbon dioxide). An oxygen deficiency hazard may arise in a laboratory environment in one of the following ways:

- By rapid release of a large quantity of asphyxiant gas into the air of a normally ventilated room. This might occur by failure of a liquid nitrogen container in a room of almost any size, a very rare event which could discharge immense volumes of gas.
- 2. By rapid release of a moderate or small quantity of asphyxiant gas into a room which is normally ventilated but small in volume. For example, the spillage of a few liters of liquid nitrogen from a handheld Dewar may result in a low-oxygen atmosphere in a small microscope room.
- 3. By slow or rapid release of asphyxiant gas into a normally unventilated room. Rooms which are normally unventilated are not suitable for activities or equipment which may discharge asphyxiant gases or carbon dioxide.
- 4. By routine release of asphyxiant gas into a room which is normally ventilated, but which has become unventilated due to a prolonged HVAC failure or power outage. Routine gas release may occur as a result of continuous boil-off during storage of cryogenic liquids, refrigerated liquid CO₂, or dry ice. Routine gas release may also occur as a result of routine work (e.g. refilling of liquid nitrogen freezers and Dewars), although as a general rule routine work shall not be conducted during HVAC failure.
- 5. By stratification of a dense asphyxiant gas near the floor, in low-lying spaces such as floor wells, or in vessels with a top opening large enough for an individual to insert their head into. Note that gases which normally have a similar density to air, or which are slightly less dense (e.g. nitrogen) may stratify if significantly colder than the surrounding atmosphere. Thus, cold nitrogen gas evolved from boiling liquid nitrogen may stratify for a time before it gradually warms up and mixes with the surrounding air.

Hazardous high-CO₂ atmospheres may arise in the same way as an oxygen deficient atmosphere. Note that to produce a given level of hazard, the required volume of gas is smaller for carbon dioxide than for simple asphyxiants.

Carbon dioxide or asphyxiant gases may enter the atmosphere of a room in one of the following general ways:

- Routine gas emission. Routine gas emission is any discharge of gas which occurs as normal part of work or equipment operation. Common sources of routine gas emission include slow evaporation of stored cryogen or dry ice, partial evaporation of cryogen when filling Dewars, and gas emission from normal work with cryogens/dry ice, such as use in cooling baths.
- 2. "Probable incidents" For the purposes of this program, a "probable incident" is an incident which may easily occur due to slight human error. The important probable incident to consider is the possibility of spilling the contents of a handheld Dewar. This is not a common occurrence but is easily foreseeable and much more probable that equipment failure. <u>LBL</u> estimates a probability of 4.6x10⁻⁴/hr for spillage and evaporation of the entire contents of a transfer Dewar.
 - Handheld transfer Dewars are most commonly around 4 L in volume; however, for the purposes of risk assessments, EH&S shall conservatively assume a default volume of 10 L for handheld Dewars. The assumption for a "probable" incident is that the Dewar is knocked over and the entire contents spills.

- Equipment failure, for example, a pressurized cryogen container may fail by a number of mechanisms, e.g. a valve breaks or a crack causes loss of vacuum insulation. <u>Lawrence Berkeley</u> <u>National Laboratory</u> (LBL) and <u>Fermilab</u> estimate probability of failure of a pressurized cryogen container as being 10⁻⁶ per hour.
- 4. Magnet quench. A cryogenically cooled superconducting magnet may quench, a process in which the magnetic field rapidly collapses and the stored magnetic energy converts to heat. The result is massive boiling of liquid helium coolant, and possibly some evaporation of liquid nitrogen in the outer Dewar. LBL and Fermilab estimate 10⁻⁶ per hour probability.
 - For the purposes of risk assessment, EH&S shall assume a magnet quench evaporates all of the liquid helium, unless evidence to the contrary is provided.
- 5. Earthquake. An earthquake could topple Dewars, cryogen storage containers, superconducting magnets, and liquid nitrogen freezers, causing widespread hazard. An earthquake can also disable building ventilation, which would prolong the intensity and duration of the hazard.

Hazard Assessment and Risk Banding

Hazard Assessment: Liquid Cryogens

EH&S will perform calculations to assess the hazard using a method based on that used by <u>LBL</u> and <u>Fermilab</u>, but simplified and adjusted for USC.

A mixing model is used to calculate atmospheric composition after a spill of liquid cryogen, using the following approximations:

- 1. Constant volume and pressure in room.
- 2. Constant air inflow into the room (equal to the ventilation rate), i.e. addition of gas to the room by evaporation of cryogen does not cause any reduction to incoming airflow.
- 3. Outflowing air (via ventilation system and leaks) increases to compensate for addition of gas to the room, thus keeping the pressure constant.
- 4. Added gas immediately and completely mixes with the atmosphere in the room.

In the case of rapid gas addition to a room (at rates which are a significant fraction of the ventilation rate), approximations 2 and 4 may become somewhat less accurate. A sufficiently rapid gas addition will slightly increase the pressure in the room which will have some effect on both the inflow and outflow of air. However, the approximations should be sufficiently accurate to be a reasonable basis for hazard assessment.

Rapid evolution of gas may cause spatial concentration variations, for example a sudden large liquid nitrogen release will initially cause higher nitrogen concentrations nearer the ground. This is not accounted for in the calculations, but may be qualitatively factored in on a case-by-case basis when reasonable to do so. For example, if a room has an extremely high ceiling then it may not be reasonable to assume gas evenly mixes with the atmosphere all the way up to the ceiling.

Unless room-specific information is available, the following default ventilation rates will be used for calculations:

- 1. Lab 4 air changes per hour
- 2. Non-lab room 2 air changes per hour

- 3. "Badly ventilated" room (i.e. few vents or very small vents) 1 air change per hour
- 4. Ventilation failure 0 air changes per hour

Following LBL and Fermilab, evaporation losses from cryogens in storage will be taken (conservatively) as 5% per day and the loss from filling a transfer Dewar will be taken as 10%. The loss from filling a pressurized storage container shall also be taken as 10%. (These percentages are based on the total volume of the vessel, not on the volume of cryogen actually present.)

For the purposes of calculation, all cryogen storage containers and liquid nitrogen freezers shall be assumed as filled to the rated capacity.

The effect of various routine and non-routine scenarios on the oxygen concentration in the atmosphere of a room will be calculated:

- Calc. 1. Equilibrium oxygen concentration. Nitrogen evolution from continuous boil-off in storage sets up a secular equilibrium with the ventilation airflow, resulting in an equilibrium oxygen value slightly lower than the normal atmosphere. The equilibrium oxygen concentration is used as the baseline for all the subsequent calculations.
- Calc. 2. Ventilation failure. This is to model a power cut or other ventilation failure. Following LBL and Fermilab, the calculation shall be based on an 8 hour ventilation failure. The ventilation rate during the shutdown shall be zero. It is assumed no work is takes place during the ventilation failure. The oxygen concentration in the room will gradually reduce due to the inflow of boil-off gas from stored liquid cryogen. The final oxygen concentration will be determined.
- Calc. 3. Failure of largest pressurized storage container. The largest single pressurized liquid nitrogen storage container in the room is assumed to fail and all the contents to escape and evaporate over 30 mins. (LB and Fermilab take one hour as the time for complete escape and evaporation of the contents.) The failure rate is taken as 10^{-6} /hour. (An analogous calculation will be done for superconducting magnets, where quench probability is 10^{-6} /hour and a quench is assumed to evaporate all the helium in 10 minutes.)
- Calc. 4. Failure of largest non-pressurized storage container. This calculation is to cover an event where a large non-pressurized storage container loses vacuum insulation, causing the stored cryogen to evaporate at a greatly increased rate. Unlike for failure of a valve or tube on a pressurized storage container, it is negligibly probable (outside of a severe earthquake) that the contents could escape en masse. For the purposes of calculation, the evaporation rate on failure of vacuum insulation is estimated as 100 L/h, although for exceptionally large vessels a bigger value may be used. The failure rate is taken as 10⁻⁶/hour (following <u>Fermilab</u>).
 - Note 1: This calculation is not used for handheld transfer Dewars, which may be tipped over and have the entire contents spilled; they are covered by Calc. 5, below.
 - Note 2: This calculation is not included in the LBL/Fermilab oxygen deficiency safety programs.
- Calc. 5. "Probable incident" usually taken to be complete spillage of the contents of the largest handheld transfer Dewar used or filled in the room. The default time assumed for complete spillage and evaporation is 10 minutes.

If liquid nitrogen is used in an unusual manner which makes some other incident easily foreseeable and likely to spill a larger volume than a transfer Dewar, then that other incident will be taken as the "probable incident".

- EH&S shall conservatively assume a default volume of 10 L for handheld Dewars, unless compelling information is provided to justify basing the calculation on a smaller volume.
- Calc. 6. Routine work. Any normal operation which results in evaporation of liquid nitrogen. The default time assumed for complete evaporation is 10 minutes, unless the nature of the cryogen application clearly justifies a longer time. The calculation will normally be based on the largest single item of routine work unless there is likelihood that several operations will be conducted simultaneously in which case the total liquid nitrogen consumption will be employed.
 - Filling of transfer Dewars, liquid nitrogen freezers, or pressurized cryogen containers

 loss is assumed to be 10% of the maximum capacity of the filled vessel (following LBL).
 - Decanting of liquid nitrogen for cooling instruments, cold traps, etc. The amount decanted will normally be assumed to completely evaporate.

The result of calculations 1, 2, 5, and 6 are the minimum oxygen concentration reached during the scenario. For calculations 3 and 4, the "fatalities per hour" calculation method of <u>LBL</u> and <u>Fermilab</u> is used. In this method, a given oxygen concentration is assigned a "fatality factor" (refer to <u>Fermilab</u> for details of the formula) which is multiplied by the probability of the incident to give an overall "fatality rate". For calculations 3 and 4, the incident probability per hour is taken as 10⁻⁶ multiplied by the number of large pressurized or non-pressurized storage vessels, respectively.

If the liquid cryogen is liquid argon, due to the high density of the gas it will be assumed to substantially stratify. To roughly model this in the calculations, an appropriately low ceiling height (e.g. 5 ft) will be employed regardless of the actual ceiling height of the room. This will greatly reduce the room volume used in the calculation, and bring it into line with the volume contained between the floor and the breathing level, in which most of the argon will be presumed to reside.

Risk Banding and Mitigation Required: Liquid Cryogens

EH&S will assess the oxygen deficiency hazard of spaces largely based on a combination of results of the above calculations, but also taking into account any special circumstances on a case-by-case basis. The following two tables (6 and 7) explain the banding system, how the calculation results translate into risk bands, and corresponding mitigation required.

Table 6. Risk bands and their meaning.

Hazard band	Meaning	Mitigation
Α	Worst case incidents cannot produce hazardous atmosphere	None.
В	Only incident which can produce a hazardous atmosphere is sudden total failure of cryogen containment or superconducting magnet quench, with a fatality rate according to the model of 10 ⁻⁷ per hour or less.	No mitigation required.
C	 Hazardous atmosphere may result from one or more of the following: Sudden total failure of cryogen containment or superconducting magnet quench, with a fatality rate according to the model of >10⁻⁷ per hour Cryogen boil-off during an 8-hour power outage "Probable incident" e.g., spillage of small Dewar of liquid nitrogen in small room (e.g., electron microscope room) Any other reasonably foreseeable cause Spaces shall also be assigned this risk category if one or more of the following is true: Routine operation is calculated to approach (but not become less than) 19.5% oxygen (when the hazard is a simple asphyxiant) Quantity of stored cryogen is sufficiently large that continuous boil-off significantly reduces the equilibrium 	Alarm and signage. In a small number of cases, if the facility would fall into band A or B but for one rare operation (e.g. filling a liquid nitrogen freezer from empty, as opposed to filling weekly), EH&S may allow (on a case-by-case basis) for no alarm to be present, provided that a safe work practice (documented in an SOP) be instituted for the rare operation. For example, requiring that the unusual filling-from-empty be conducted extra-slowly with doors open and a portable oxygen sensor on hand.
C2	oxygen concentration Spaces which receive piped liquid nitrogen from large external storage tanks, e.g., automatically-refilled liquid nitrogen freezer farms.	Alarm and signage. Automatic shut-off valves may also be required. Emergency ventilation systems may be required for large installations.
D	Routine operations have significant potential to create hazardous atmosphere, for example a liquid nitrogen filling station in an excessively small room, or liquid nitrogen boil-off from cryogen storage in an inadequately ventilated room. Depending on the specific calculation results, a facility in hazard band D may be deemed unacceptable if routine work has a high probability or certainly of causing frequent alarm activation. In such cases, redesign may be required to lower the risk, for example by relocating cryogen to other locations. In other cases, a band D facility may be acceptable with specific facility modification or workarounds. For example, if a location is assessed as hazard band D based on the filling of a large liquid nitrogen freezer from empty, then a second calculation may be performed to see what oxygen levels are likely from a more usual work practice of filling the freezer weekly. If this calculation gives an acceptable non-hazardous atmosphere, the facility will be kept in band D but a facility-specific workaround may be allowed for the "rare routine" operation of filling the freezer from empty, to prevent alarm activation in that event.	Alarm and signage and facility-specific safe work practices (documented in an SOP), or facility redesign, or relocation of hazard Example of redesign: Removing the door from a very small room containing a liquid nitrogen filling station or replacing it with a fully-louvred door. Example of workaround: A facility falls into category D due to the "rare routine" operation of filling a liquid nitrogen freezer from empty, but recalculation based on the usual procedure of filling the freezer weekly results in a hazard band of C. An SOP is instituted for the rare operation of filling from empty, which may include such work practices as extra-slow filling. Signage forbidding filling from empty without appropriate precautions and permission from the facility manager would also be required.

Table 7. Relationship between calculation results and risk band assignment for simple asphyxiants.

Scenario or	Calc. % O _{2,}	Risk	Comments and Mitigation required
Condition	[fatalities h ⁻¹]	band*	
1. Equilibrium oxygen	≥20.4	А	None.
concentration	<20.4 and ≥19.5	С	Liquid nitrogen storage under conditions where the scale of continuous boil-off will cause reduced oxygen concentrations in this range is concerning. A low oxygen alarm and signage are required. Towards the bottom of the range (<20.2%), serious consideration should be given to redesign of the facility (e.g. reduced volume of liquid nitrogen, increased ventilation) otherwise frequent alarm activation will be a problem.
	<19.5	D	Unacceptable. Facility must be redesigned to take it out of this risk band.
2. Ventilation failure	≥19.5	А	None
(8h)	<19.5	C	Alarm and signage.
3. Failure of largest	≥19.5	A	None
pressurized	<19.5 and [<10 ⁻⁷]	В	None
storage container	[>10 ⁻⁷]	C	Alarm and signage.
4. Failure of largest	≥19.5	A	None
non-pressurized	<19.5 and $[\le 10^{-7}]$	B	None
storage container	[>10 ⁻⁷]	C	Alarm and signage.
5. "Probable	≥19.5	A	None
incident"	<19.5	С	Alarm and signage. If the room is very small and oxygen levels can drop severely (e.g. <17%), consider additional restriction on the size of transfer Dewar which can be taken into the room.
6. Routine work	≥20	А	None
	<20 and ≥19.5	С	Alarm and signage. Consideration should be given to redesigning facility so routine work cannot reduce oxygen levels to this extent, otherwise frequent alarm activation will be a problem.
	<19.5	D	Case 1: Frequent routine work results in likely <19.5 % O ₂ . Unacceptable. Facility shall be redesigned to take it out of this risk band.
			Case 2: Frequent routine work (e.g. weekly filling of liquid nitrogen freezers) results in likely ≥19.5 % O ₂ but "rare routine" work (e.g. filling of liquid nitrogen freezer from empty) results in likely <19.5 % O ₂ . Redesign facility to take it to a lower risk band, OR, on a case-by-case basis, EH&S may permit an alarm and signage to cover the frequent routine work and a documented safe work practice to limit the hazard posed by the "rare routine" operation.

Scenario or	Calc. % O _{2,}	Risk	Comments and Mitigation required			
Condition	[fatalities h ⁻¹]	band*				
Liquid nitrogen piped into room from external tank	N/A	C2	Alarm and signage. Automatic shut-off valves may also be required. Emergency ventilation systems may be required for large installations.			
* Overall risk band for a D>C2>C>B>A.	* Overall risk band for a space is the highest-hazard risk band for any of the individual scenarios, where					

Hazard Assessment: Carbon Dioxide

Carbon dioxide installations, especially those in small rooms or closets, or those which use refrigerated liquid cylinders, or which have multiple room-temperate high pressure cylinders manifolded together, will be assessed on a case-by-case basis by EH&S to determine whether or not an alarm system is required.

Any dry ice storage discovered in rooms which are small or may be inadequately ventilated will be assessed by EH&S. In general, rather than completing a detailed risk assessment, the dry ice will be required to be permanently moved to a more suitable area. If there is a compelling technical reason why dry ice has to be used or stored in a poorly ventilated space, EH&S can conduct a risk assessment to determine if an alarm system is required. EH&S may require removal of the dry ice pending either the risk assessment showing acceptably low hazard, or installation of an alarm.

Hazard Assessment: Freezer Backup Systems

Electromechanical freezers are sometimes fitted with a liquid nitrogen or carbon dioxide backup system to provide active cooling in the event of a power cut or failure of the primary refrigeration system. When a refrigeration failure occurs, the backup system is activated by a battery powered control box which operates a valve connected to a source of liquid CO₂ or liquid N₂. The liquid coolant is intermittently sprayed into the interior of the freezer at an appropriate rate to maintain the contents at a low temperature.⁶ Backup systems may be integrated into the freezer or may be fitted as an optional accessory.

Liquid N_2/CO_2 consumption depends on freezer temperature, freezer size, insulation efficiency, and the ambient temperature of the room. Typical systems use 8-10 lb/h of CO₂ or 4.5-5.6 L/h liquid N_2 (e.g. Thermoscientific TSX series ultra-low temperature freezers).

Where possible, freezers should be backed up by emergency power in preference to using CO₂/N₂ systems. This is partly to eliminate possible asphyxiation/CO₂-toxicity hazards, and also because CO₂/N₂ systems are regarded as unreliable. For example, the <u>University of Melbourne Design Standards</u> states "CO₂ backup systems are not recommended because they are not generally reliable. Freezer Temperature Monitoring with remote alarming provides sufficient early notification to prevent spoilage, should a refrigeration problem occur."

⁶ Some older CO_2 backup systems might dump all the CO_2 into the freezer in one go, resulting in a mass of dry ice which will keep the freezer cool for a few hours.

When liquid nitrogen in pressurized cylinders is used as the backup cooling agent it has the disadvantage that continuous boil-off occurs, necessitating the cylinders be refilled at regular intervals. Liquified carbon dioxide can be stored in room temperature high pressure cylinders without boil-off losses.⁷ The cylinders must be siphon cylinders (also known as dip-tube cylinders), where the cylinder valve is connected to an internal tube which takes liquid from the bottom of the cylinder. A regular carbon dioxide cylinder where gas is taken from the vapor space at the top of the cylinder will not function if attempt is made to use it for freezer backup.

When high-pressure liquid carbon dioxide at room or near-room temperature is sprayed into a freezer, the phase behavior of CO₂ causes a proportion of the liquid to almost instantly flash into gas, with the reduction in temperature being sufficient to freeze the remainder into a fine spray of powdered dry ice (frozen CO₂). Liquid CO₂ cannot exist at atmospheric pressure; see Appendix for details of carbon dioxide phase behavior.

 CO_2/N_2 freezer backup systems have potential to pose a significant low- O_2 /high- CO_2 hazard. When operating, gas is vented directly out of the freezer into the atmosphere of the room. If a number of freezers in the same room are all fitted with liquid N_2/CO_2 backup systems and a power cut occurs, all the freezers will start venting gas into the room simultaneously. At the same time, assuming the freezer's power was not interrupted by a local fault, the building ventilation system will be inoperative due to the power cut. Furthermore, if the power cut is prolonged, research personnel may be tempted to enter the room to retrieve valuable samples. Thus, a situation of substantial low- O_2 /high- CO_2 hazard and risk may ensue.

EH&S will assess, on a case-by-case basis, the hazard in spaces where CO₂/N₂ freezer backup systems are present. Calculation will be based on a prolonged power cut where there is no ventilation and all of the cooling gas is released. If the resulting atmosphere is hazardous then a low oxygen and/or high carbon dioxide alarm will be required. Due to the particular hazards posed during power cuts, and the potential temptation for researchers to enter the room during that period, the alarm will need to be on a backup power supply of suitably long endurance. Appropriate signage will also be required to dissuade entry during a power cut.

When freezers using liquid CO_2/N_2 backup are plugged into emergency power the probability of all the freezers simultaneously losing power is greatly reduced. This does not obviate the need for an alarm if calculations indicate that a hazardous atmosphere is possible.

Hazard Assessment: Simple Asphyxiant Gas Cylinders in Unventilated Closets and Basement Rooms As mentioned in the section "Hazards Outline", above, due the relatively limited gas volumes contained in high pressure cylinders of simple asphyxiants, the potential to create a low oxygen hazard is in general significantly lower than for liquid cryogens. Furthermore, whereas cryogens are easily spilled, resulting in quick evolution of large volumes of gas, similarly rapid escape of large gas volumes from gas cylinders is a very uncommon incident.

⁷ Minor leak can occur. It is recommended to change the cylinders annually, or to keep a log of their weight when new and annually thereafter, to ensure they are always full.

Therefore, only a minority of installations using high pressure cylinders of simple asphyxiants will need to be assessed by EH&S. Risk assessments will be done on a case-by-case basis.

Gas cylinders shall NOT be stored in unventilated basement rooms without specific dispensation from EH&S.

Unventilated closets containing high pressure gas cylinders of simple asphyxiants generally do not require risk assessment, or alarms or other mitigation, if they are sufficiently small or shallow that a person cannot practically fit inside with the door closed. Larger unventilated closets containing high pressure gas cylinders of simple asphyxiants do not need to be risk assessed unless they contain multiple cylinders manifolded together, contain exceptionally large numbers of cylinders, or unless personnel work in the space for extended periods of time. Risk assessments will be conducted by EH&S on a case-by-case basis. Mitigation measures, where required, may include one or more of the following:

- Gas alarm or low oxygen alarm
- Removal of the door closer and replacement by a door opener
- Removal of anything in the space (e.g., instrumentation) which is causing it to be used as a workspace and occupied for extended periods of time
- Removal of internal light or installation of a door operated switch to turn the light off when the door is closed (to enforce keeping the door open when the closet is occupied)
- Removal of door
- Fully louvred door
- Signage

3.0 ALARMS AND SIGNAGE REQUIREMENTS

Alarms

Alarm systems shall be installed in accordance with EH&S requirements and shall meet applicable codes, standards, and permitting requirements. In particular, alarm systems shall meet the requirements of the Los Angeles Fire Code (2020 edition at time of writing). Specific alarm requirements will depend on the particulars of the facility and will be determined by an EH&S risk assessment. Installation of alarm systems should be project-managed by FPM to ensure code and permitting requirements are met. Complex alarm systems, especially those for facilities where liquid nitrogen is piped from a large external tank, may need to be designed by appropriately qualified engineers with expertise in gas and cryogen safety systems.

Carbon dioxide alarms should warn at the PEL (5000 ppm or 0.5% CO₂) and alarm at an appropriate level between twice the PEL (10,000 ppm or 1% CO₂) and the STEL (30,000 ppm or 3%).⁸

⁸ The 2020 Los Angeles Fire Code mentions carbon dioxide alarms in the parts of Section 5307 which cover certain beverage dispensing systems and atmospheric enrichment systems. 5307.3.2 and 5307.4.3 specify when and where CO_2 sensors are required, that "carbon dioxide sensors shall be provided within 12 inches (305 mm) of the floor", and provide for specific low level and high level alarm functions. For example, 5307.3.2, which applies to the beverage dispensing systems, states "... The system shall be designed as follows:

^{1.} Activates an audible and visible supervisory alarm at a normally attended location upon detection of a carbon dioxide concentration of 5,000 ppm (9000 mg/m³)

10,000 ppm should be the usual setpoint, but it may be raised with EH&S approval, up to a maximum of 30,000 ppm, if a setpoint of 10,000 ppm results in an excessive number of false alarms. Low oxygen alarms shall sound the local annunciator at a 19.5% oxygen setpoint. If the alarm is wired into the building system and the facility contains sufficient cryogen to potentially pose a widespread hazard, it may be appropriate for a second lower setpoint (e.g., 18%) to trigger a floor- or building-wide evacuation.

Depending on the particulars of the facility, EH&S may require merely require a local alarm with a horn-strobe unit inside the room, a horn-strobe inside the room and second outside the door, or may require the alarm to be interconnected with the building alarm system. Strobes shall be blue and the alarm shall be continuous tone, unless EH&S has given specific dispensation to the contrary. Sensors shall be an appropriate distance from the ground considering the density of the gas. Depending on the particular facility, one atmospheric sensor may suffice or a number of sensors may be required.

Alarm systems shall be maintained according to manufacturer's recommendations, including periodic calibration/bump testing and sensor replacement. In no case shall calibration or testing be less than annually. All calibration, maintenance, and testing shall be recorded in a logbook or tracked by some other suitable recordkeeping method. Records shall be viewable by EH&S on request, for example, during annual lab inspections.

Carbon Dioxide vs. Low Oxygen Sensors

Where the hazard within a room is carbon dioxide and EH&S determines than an alarm is required, the alarm type shall be a carbon dioxide alarm. Low oxygen alarms are not generally an acceptable substitute for monitoring a carbon dioxide hazard within a room.

When a carbon dioxide hazard exists within a small closet as opposed to a room and EH&S determines that an alarm is required, it may be permissible on a case-by-case basis to employ a low oxygen sensor rather than a carbon dioxide sensor. The reasoning behind this is that a closet is not a space which is likely to be occupied by an individual other than when changing gas cylinders, and then only with the door open. At all other times the door should be closed (and signed to that effect). Due to the small volume of the closet, if there were to be a carbon dioxide leak, the concentration within the closet should rise sufficiently to activate a low oxygen alarm (19.5% O₂, 69,200 ppm CO₂) long before any hazardous CO₂ concentration could form in an adjacent room or corridor. This above exception is mainly aimed at giving EH&S case-by-case discretion to allow pre-existing low oxygen alarms within carbon dioxide storage closets to remain. In new installations, carbon dioxide alarms are to be preferred.

Carbon dioxide sensors usually detect the gas through its infrared absorption. IR carbon dioxide sensors have a longer lifetime than electrochemical oxygen sensors, though unfortunately the CO₂ sensors have a higher upfront cost.

^{2.} Activates an audible and visible alarm within the room or immediate area where the system is installed upon detection of a carbon dioxide concentration of 30,000 ppm (54,000 mg/m³)"

In the absence of interferences, infrared based CO₂ sensors should be more reliable and have a lower false alarm rate than electrochemical oxygen sensors. Sources of organic vapors should be kept away from CO₂ sensors to avoid possible false alarms due to the strong IR absorption by organic molecules.

Signage: Cold Rooms

Almost all cold rooms at USC are non-ventilated. Introduction of liquid nitrogen or dry ice into non-ventilated cold rooms poses significant risk of creating a hazardous atmosphere. All non-ventilated cold rooms shall be clearly signed to forbid introduction of dry ice or liquid nitrogen. Signage shall be approved by EH&S, compliant with <u>8 CCR §3340</u>, and prominently displayed on the door of the cold room.

Ventilated cold rooms shall also be signed against introduction of dry ice or cryogens unless exempted by EH&S on a case-by-case basis.

Signage: Alarmed Rooms

All rooms which are fitted with a low oxygen alarm or a carbon dioxide alarm shall be prominently signed inside and outside the room. The signage shall be of a design and wording approved by EH&S. A representative example of wording which might be approved is the following:

- Signage inside the room:
 - 1. This room is fitted with a low oxygen alarm / carbon dioxide alarm
 - 2. Alarm sounds like [continuous tone]
 - 3. IMMEDIATELY EVACUATE ROOM IF ALARM SOUNDS
 - 4. Close door behind you and notify DPS.
- Signage outside the room:
 - 1. This room may develop a hazardous [oxygen deficient / high carbon dioxide] atmosphere and is fitted with a low oxygen alarm / carbon dioxide alarm
 - 2. Alarm sounds like [continuous tone]
 - 3. If alarm is sounding:
 - Do NOT open the door or attempt to enter room
 - Do NOT attempt to rescue anyone trapped in the room
 - *Notify DPS on 213-740-4321 / 323-442-1000* [include the number appropriate for the campus]
 - 1. Do NOT open door or enter room during a power cut or ventilation shutdown.

4.0 SEISMIC REQUIREMENTS

An earthquake may result in cryogen release in a number of ways:

- Open-topped Dewars, freezers, or superconducting magnets may fall over.
- A pressurized cryogen container may fall over. The container will likely not split open (they are constructed to a certain standard of robustness), but valves or pipework may be broken. Even if the container and valves are intact, cryogen is still likely to escape from a container on its side since the pressure relief vent which discharges boil-off gas may now lie under the liquid level. If this happens, the container will begin venting cryogenic liquid via the pressure release valve.
- Freezers and other heavy items plumbed into a liquid nitrogen supply may move and break the pipe.

All items containing significant quantities of cryogenic liquid should be adequately restrained to prevent damage or tipping in event of earthquake. The <u>USC Chemical Hygiene Plan</u> (Section 4) contains the following general guidance:

"Cryogenic liquid storage devices are an immediate asphyxiation hazard if there is a large spill or breach of containment.

Therefore:

- "Large" (multi-liter) liquid nitrogen Dewars must be secured against tipping.
 - Dewars come in all shapes and sizes; therefore, a precise definition of "large" is not practical to define. In general, any Dewar too large to be carried should be restrained, unless extremely short and wide-based.
 - Possible restraining methods include securely chaining to the wall, bolting to the floor, or using a purpose-built steel rack. In the case of chains, a tall Dewar can be restrained by two chains passed around the body in a like manner to how gas cylinders are restrained. For shorter Dewars, a more practical method may be to use a very short chain to affix the handle to the wall.
- Pressurized cryogen storage containers must be secured regardless of size.
- Liquid nitrogen freezers should be restrained."

Seismic restraint of heavy items such as NMR machines and large liquid nitrogen freezers should be designed in accordance with sound engineering practice. Seismic restraint of heavy items may be governed by codes and standards; consult an FPM Project Manager for guidance. An engineer may be required to design restraints to the required specifications.

5.0 EMERGENCY RESPONSE

Responsibility

The USC EH&S Hazardous Materials Manager has final responsibility for determining appropriate emergency response procedures for dealing with low-O₂/high-CO₂ alarm activation and other carbon dioxide or simple asphyxiant related incidents.

SOPs

PIs or facilities managers who have oversight of low-O₂/high-CO₂ alarmed spaces shall have an SOP providing basic details of the alarm system and response, including work and home contact details of key personnel. SOPs shall be shared with EH&S. SOPs shall be kept up to date and shall be re-sent to EH&S after each revision.

Alarm Activation

In the event of low-O₂/high-CO₂ local alarm activation, personnel shall:

- 1. Immediately evacuate the room.
- 2. Ensure the door is closed after the last person has exited
- 3. Notify DPS
- 4. Notify other key personnel in accordance with the facility-specific response SOP

- 5. Initiate building evacuation (using hazardous gas pull station or fire alarm) if advised to do so by DPS or Hazmat, or if the incident is catastrophically large and the hazard might extend beyond a single room.
- 6. Prevent entry to the area even if the alarm ceases sounding
- 7. All personnel having knowledge of the incident should stay on-site so they can provide first-hand information to first responders (LAFD or USC Hazmat)
- 8. Re-entry to the area shall NOT be attempted until LAFD or USC Hazmat has determined that the area is safe and has given explicit permission for personnel to enter.

APPENDIX. SUPPLEMENTAL INFORMATION

Unit 1 Unit 2 To convert from units 1 to 2, multiply by: Pounds Grams 453.59 Cubic feet 28.317 Liters Bar Pounds per square inch 14.504 torr mmHg 1 millbar torr 1.333 Ref: CRC Handbook of Chemistry and Physics, 72nd Edition, 1991.

Table 8. Useful conversion factors.

Note: For the purposes of this table, values have been rounded. Please refer to the CRC Handbook if high precision conversion factors are required.

Table 9. Relevant cryogen and dry ice properties.

Prop	erty	Liquid helium	Liq. nitrogen	Liq. argon	Solid carbon dioxide (dry ice)
Boiling point at normal	atmospheric	−269°C	–196°C	–186°C	-78.5°C (sublimes)
Liters of gas from	pressure Liters of gas from gas volume at 15 °C		682	822	845
boiling/sublimation of one liter of liquid/solid	gas volume at 70 °F	754	696	841	[not given in ref. 2]
Approximate gas densi the same temperature	7x less dense	About equal	1.4x denser	1.5x denser	
Liquid density at norma	125 0.276	808 1.78	1394 3.073	1564 (solid)	
Latent heat of sublimation point /	01	21	199	163	573

SIMPLE ASPHYXIANTS AND CARBON DIOXIDE PROGRAM: HAZARDS, RISK ASSESSMENT, AND MITIGATION

Property	Liquid helium	Liq. nitrogen	Liq. argon	Solid carbon dioxide (dry ice)		
Refs: 1) <u>https://www.boconline.co.uk/en/images/care-with-cryogenics_tcm410-39400.pdf</u> 2) <u>http://airgassgcatalog.com/catalog/ap017.pdf</u>						

Table 10. Gas densities and gas volume per liter of cryogen evaporated.

Property	Values are given for gas at 70°F, atmospheric pressure					
	Helium	Nitrogen	Argon	Carbon dioxide		
Density / lb / cu. ft	0.0103	0.0725	0.1034	0.1142		
Specific volume / cu. ft / lb	96.65	13.80	9.67	8.76		
Cu. ft of gas from evaporation of 1	26.6	24.6	29.7	N/A		
L of cryogen						
Refs: 1) <u>http://www.airproducts.com/products/Gases/gas-facts/physical-properties/</u> ; 2) CO2 specific						
volume is taken from http://catalogs.praxairdirect.com/i/34012-solutions-guide/50 ; density is						
calculated from that. Ref. 1 gives a slightly less conservative value of 8.74 cu. ft / lb and density of						
0.1144 lb / cu. ft.						

Common Asphyxiant and Carbon Dioxide Forms of Supply

Nitrogen, Argon, Helium

Nitrogen, helium, and argon are the most common simple asphyxiant gases at USC. All three substances are met with in high pressure cylinders and in the form of cryogenic liquid, though liquid argon is uncommon (present in only one space at USC at time of writing).

Using data taken from Praxair, these are some typical quantities which may be encountered:

Gas cylinders:

K-size steel cylinders (51in high, 9 in wide; a common size at USC) have the following gas capacities (cu. ft) at 2200 psig fill pressure (measured at 70°F/21°C): Nitrogen 228; Argon 248; Helium, 213. Larger T-size cylinders (55 in high, 9.25 in wide), also common at USC, have the following gas capacities (cu. ft) at 2640 psig fill pressure (measured at 70°F/21°C): Nitrogen 304; Argon 335; Helium 286. Note: Other gas supplies may use a different designation for K- or T-size cylinders, see <u>online table</u> for more information.

Cryogenic Container Sizes

Liquid helium uses different cryogenic containers to liquid nitrogen/argon and is not covered here. Common sizes of nitrogen/argon pressurized cryogenic containers are given in Table 11, below.

Table 11. Common cryogenic container sizes for nitrogen and argon.

Property	Cryogenic Container Size / Liters							
	160	180	200	230	230	265		
Height / in	60-61	64	66	53	61.5	58		
Dia. / in	20	20	20	26	24	26		
N ₂ capacity cu. ft*	3936	4428	4920	5658		6519		
Container size and dimensions taken from <u>http://catalogs.praxairdirect.com/i/34012-solutions-guide/50</u> and <u>http://www.airproducts.com/~/media/Files/PDF/company/safetygram-27.pdf</u>								
Note: Common pres 230 and 350 psig are		•						

operations should be at 22 psig or below.

* Approximate maximum nitrogen capacity based on 1 L liquid N₂ boiling to 24.6 cu. ft of gas. The actual capacity depends on the pressure of the container. The capacity decreases slightly with increasing pressure, for example a 160 L container holds 3,930 cu. ft at 22 psig, 3,690 cu. ft at 230 psig, and 3,470 cu. ft at 350 psig.

More information on cryogenic containers and cryogenic container safety:

- <u>http://www.airproducts.com/~/media/Files/PDF/company/safetygram-27.pdf</u>
- <u>https://www.chartindustries.com/Industry/Industry-Products/Packaged-Gases/Dura-Cyl-Liquid-Cylinder</u>
- <u>http://files.chartindustries.com/10642912 Liquid Cylinder Product Manual ws.pdf</u>
- <u>https://www.ncnr.nist.gov/equipment/cryostats/CryogenSafety.pdf</u>

Carbon Dioxide

Before presenting the formats in which carbon dioxide is supplied, it is worth reviewing the phase behavior of this material: At atmospheric pressure, solid carbon dioxide sublimes directly to gas, but under pressures above 5.2 bar, liquid carbon dioxide can exist at temperatures between –56.6 and +31.1°C. Above the critical temperature of 31.1°C, carbon dioxide exists only in the gaseous phase. At temperatures below –56.6°C, carbon dioxide exists as a gas or a solid, depending on temperature and pressure; there is no liquid phase below –56.6°C.

(https://www.linde-gas.pt/en/images/Safety_Advice_12_tcm303-25938.pdf)

Carbon dioxide is supplied in the following formats:

- Dry ice. At atmospheric pressure, solid carbon dioxide ("dry ice") sublimes at -78.5°C, that is to say, it evaporates directly to gas without passing through a liquid phase. This property makes dry ice an extremely convenient cooling agent, and it is a common material at USC. 1 lb of dry ice evaporates to give 8.76 cu. ft of gas.
- 2. High pressure cylinders. Liquid carbon dioxide is supplied in ambient-temperature cylinders containing liquid CO₂ under a pressure of 45-65 bar, depending on temperature.⁹ Carbon dioxide is sold by weight, not gas volume. A K-size steel cylinder contains 64 lb carbon dioxide when full,

equivalent to 561 cu. ft of gas.

https://www.linde-gas.com/en/images/LMB_Safety%20Advice_01_tcm17-165650.pdf

3. Refrigerated liquid. Carbon dioxide is supplied in insulated containers (similar to those used for liquid nitrogen) containing refrigerated liquid at temperatures between -35°C and -15°C and pressures of 12 to 25 bar. The insulated containers vent boil-off gas to the air through a pressure-release valve. Refrigerated liquid is a common way to supply bulk carbon dioxide to industry; it is less common in labs than ambient temperature CO₂ cylinders, but is met with in a few locations at USC where demand for carbon dioxide gas is particularly high. https://www.linde-gas.com/en/images/LMB_Safety%20Advice_01_tcm17-165650.pdf

Other Simple Asphyxiants

Other asphyxiant gases are most commonly supplied in gas cylinders. Many gases (e.g. SF₆, refrigerant HFCs) have critical temperatures above room temperature, meaning the cylinders will contain liquefied gas. Simple asphyxiants, other than the cryogenic liquid forms of nitrogen, helium, and more rarely argon, are unlikely to be present in sufficient quantities to pose a significant oxygen deficiency hazard in a normal size lab. However, hazard may arise from the presence of gas in small spaces or unventilated spaces. Also, the extremely high density of some of the less common simple asphyxiants (e.g. SF₆) makes them particularly hazardous in low lying areas or vessels with a top opening large enough to lean into.