CHAPTER

ELEVEN

SAFETY

F. J. Edeskuty and M. Daugherty

MS-J576, LANL, Los Alamos, NM 87545

11-1 INTRODUCTION

Safety is primarily important in cryogenic engineering to protect personnel and property. A secondary reason for the importance of safety is that cryogenic equipment can be very expensive. To ensure the safety of a cryogenic project it is necessary that the system be designed and constructed to be as safe as possible and that it be operated safely. Safe operation of a cryogenic system requires that the operation be thoroughly understood and that attention to safety practices is strictly followed. Past experience with operations that do not include the use of cryogenic fluids is not sufficient because the properties of cryogenic fluids and materials can vary considerably over the range of temperature from ambient temperature down to operating temperatures. For the design of the system and its operation, a thorough knowledge is required of all of the physical principles involved. Also, thorough and continuing training of operators is necessary [1].

11-2 SOURCES OF HAZARDS

In working with any cryogenic fluid, hazards that can arise include those that are physiological and those that originate from physical (or mechanical) behavior of the fluids themselves or the structural materials in which they are contained. If work involves a combustible cryogen or a combustion-enhancing substance like oxygen or oxygen-enriched air, unwanted fires or even explosions can also be a concern [1].

11-3 PHYSIOLOGICAL HAZARDS

Physiological hazards arise because of the very low temperatures of the cryogens, which can cause freezing of human tissue or hypothermia. Also of concern is the very large expansion of cryogenic fluids as they evaporate with the resultant gas warming to ambient temperature (on the order of a thousand-fold multiplication in volume). Toxicity can give rise to an additional hazard, although with the more commonly encountered cryogens (oxygen, nitrogen, hydrogen, and helium) this is not a problem.

11-3-1 Cold Damage to Living Tissue

The very cold temperatures of all cryogens is an obvious hazard if the fluid is allowed to come into contact with human tissue. Such contact can result in almost instantaneous freezing, and the resulting damage to the tissue is in some respects similar to a thermal burn. Thus the term "cryogenic burn" is often encountered. Although it is of obvious importance to prevent contact with either the liquid cryogen or the cold gas accompanying the liquid, an equally important precaution is to preclude the possibility of contact of flesh with any cold metal that is at cryogenic temperatures. A typical place where such cold metal might be encountered is in the vent system through which cold vapors could be passing. Obvious precautions include such measures as locating all ports where cryogenic fluids or cold vapors could be released in places where these fluids could not possibly impinge upon personnel. An equally important precaution is that of thermally insulating any cold part of the system so that cold surfaces are not exposed where they could be inadvertently touched.

In working with systems at cryogenic temperatures, protective clothing should be worn. Because the eyes are especially vulnerable, face shields or goggles should be used. As much of the body as practical should be covered by wearing long-sleeve shirts and long trousers with pant legs not being tucked into boots. Thermally insulating gloves should also be worn.

Contact with cold fluids or cold metal can freeze human tissue extremely fast. Freezing occurs when the tissue is cooled to a temperature of about −3 °C (below 0 °C because of the freezing point lowering as a result of dissolved solutes). If, in spite of the necessary precautions being taken, a freezing of tissue should occur, first aid treatment should consist of making the patient comfortable, gently removing any covering clothing (taking care not to tear any skin), and then gently warming the frozen part, preferably by immersion in warm water (40 to 42 °C, not above 44 °C). Medical attention should promptly be sought [2].

Cold temperatures can harm human beings even if no tissue is frozen. Body heat is maintained by metabolism, muscle action, and shivering. If the body can not generate heat at the rate the heat is being removed, body temperature will continuously decrease, and hypothermia can result. If the body core temperature drops below 35 °C, a general deterioration of the functioning of the body organs can occur as well as that of the nervous, cardiac, and respiratory systems. At temperatures below 28 °C, ventricular fibrillation becomes more likely [3]. In most cases, a person in an environment where hypothermia could be a problem can leave or escape. However, care should be taken to prevent situations in which a person might not be able to escape a rapid flow of exhausting cryogenic fluid, either because of the lack of an available exit or because of being rendered physically incapable of leaving. For this reason it is advisable to provide more than one path of egress from an experimental site and to forbid workers from working alone where a possibility of cold venting fluid could exist.

Table 11-1 Change in volume from liquid at normal boiling point to ambient temperature gas at 1 atmosphere

Substance	Ratio V_{gas}/V_{liquid}
Helium	701
p-Hydrogen	788
Neon	1341
Nitrogen	646
Argon	779
Oxygen	797
CO_2	762

11-3-2 Asphyxiation

Table 11-1 illustrates the large expansion that occurs when a given volume of cryogenic liquid evaporates and is warmed to ambient temperature. The table indicates that a relatively small quantity of a liquid cryogen, other than oxygen, can either displace, or at least dilute, the breathable atmosphere in a location near the spill of the liquid. This becomes even more hazardous in a closed location such as a small room. Table 11-2 gives the consequences of oxygen depletion. However, these results must be taken as only an indication because there are differences in the response from one person to the next. Also, local atmospheric pressure can play a part. The important point is that depletion of the atmosphere to the point where the oxygen concentration is less than 19.5% has been classified as an oxygen deficient atmosphere [4].

Oxygen depletion is a serious hazard. It is even more insidious because one symptom of anoxia is a general feeling of well being, or even euphoria, with the consequence that in this condition a person might not even try to extricate himself or herself from a hazardous location. A particularly dangerous situation for oxygen depletion is in the entry of personnel into tanks. This should never be attempted without a thorough, well-thought-out safety plan, including a method of removing a person, if necessary, without endangering an additional person. Even in the outdoors a hazardously depleted

Table 11-2 Symptoms and effects of oxygen deficiency (from Ref. [4])

Oxygen content (volume %)	At rest symptoms and effects
15–19	Possible impaired coordination; may induce early symptoms in persons with lung, heart, or circulatory problems.
12–15	Deeper respiration, faster pulse, and impaired judgment, coordination, and perception.
10–12	Further increase in respiration depth and rate, lips blue, poor coordination, and judgment.
8–10	Nausea, vomiting, ashen face, mental failure, fainting, unconsciousness.
6–8	4–5 minutes, all recover with treatment; 6 minutes, fatal in 25 to 50% of cases; 8 minutes, fatal in 50 to 100% of cases.
4–6	Coma in 40 seconds and then convulsions, breathing failure, and death.

concentration of oxygen can persist, especially in low areas where the colder, more dense gases may be slow to disperse. Precautions against the hazard of oxygen depletion include limiting the amount of cryogenic fluid within enclosed spaces where personnel can be present, and oxygen monitoring.

11-3-3 Toxicity

Although carbon dioxide is not toxic (and usually not considered a cryogen), it is worth mentioning that an atmosphere with too much carbon dioxide can not allow the body to get rid of the carbon dioxide that is formed by normal respiration. Breathing of an atmosphere with 10% carbon dioxide can result in unconsciousness in less than 1 minute. An upper limit of 5000 ppm has been established for an 8-hour work day [5].

The truly toxic cryogens are carbon monoxide, fluorine, and ozone. Carbon monoxide has an affinity to combine with the hemoglobin in the blood that is 300 times as great as that of oxygen. Thus the body is starved of oxygen by chemical asphyxia. Breathing an atmosphere with 4000 ppm can result in death in less than 1 hour [6]. An upper limit for a 40-hour work week has been established at 25 ppm [7].

Fluorine presents a hazard by inhalation as well as from contact with the skin, where it can cause burns. The exposure limit is 1 ppm for a 40-hour work week. Fluorine's pungent odor allows the human nose to be a good detector, for it can detect concentrations down to about 0.14 ppm [8]. Ozone is also toxic and is presumed to be fatal at concentrations above 50 ppm. The upper limit for human exposure has been placed at 0.1 ppm [9].

11-4 PHYSICAL (OR MECHANICAL) HAZARDS

Physical hazards result from the effect of the low temperatures on structural materials being used to contain the cryogens and from some of the properties of the cryogens themselves.

11-4-1 Embrittlement

Cold temperatures can embrittle some materials at temperatures much warmer than those of cryogens. Recent investigations of the steel from the Titanic have shown that cold embrittlement may have played a part in the massive damage to that vessel in the cold iceberg environment of the North Atlantic Ocean. A cryogenic example of embrittlement is that of the rupture of a tank containing liquefied natural gas (LNG) in Cleveland, Ohio, in 1944. The steel chosen for this structure contained 3.5% nickel. This material has been shown to become brittle at the temperature of LNG (about 110 K). The tank rupture spilled over 4000 m^3 and resulted in over 100 deaths and 200 injuries [10].

An insight into the mechanism for cold embrittlement can be obtained from the behavior of the yield and tensile stresses of a material as a function of temperature. Figure 11-1 shows the behavior of an aluminum alloy that is a good material for cryogenic applications. As the temperature is lowered, the tensile strength increases at a greater rate than does the yield strength. Thus, the difference between these two parameters, which is an indication of ductility, also increases as temperature is lowered. Figure 11-2,

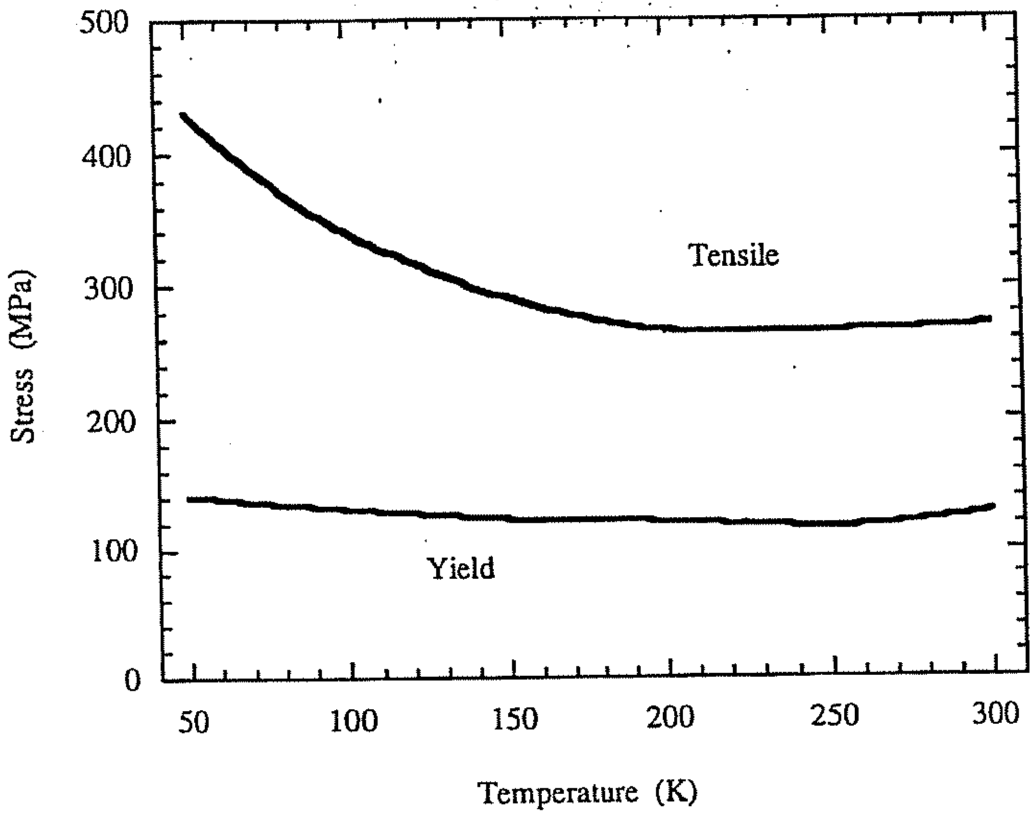

Figure 11-1 Tensile and yield strength of 5086 aluminum.

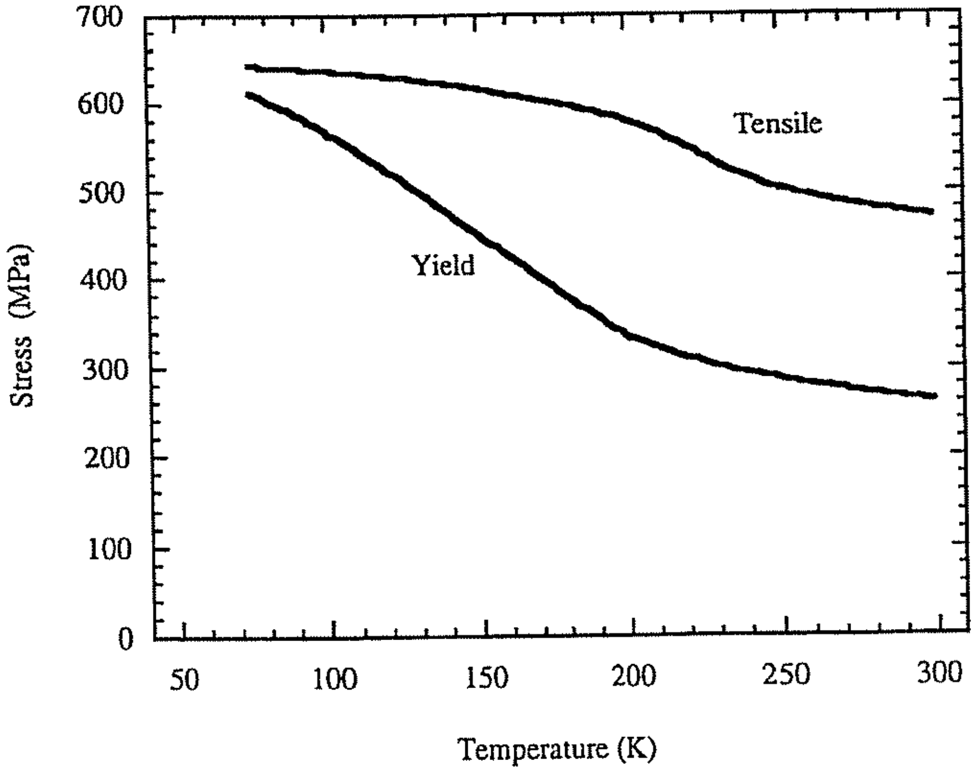

Figure 11-2 Tensile and yield strength of 430 stainless steel.

Table 11-3 Effect of hydrogen exposure on the ultimate strength of various materials

Material (notched samples)	Exposure (at 300 K)	Strength (MPa)
4140 (high strength)	69 Mpa N_2	2496
	14 MPa H_2	931
	41 MPa H_2	834
4140 (low strength)	69 Mpa N_2	1660
	41 MPa H_2	1427
	69 MPa H_2	1407
K Monel PH	69 MPa N_2	1731
	69 MPa H_2	779
K Monel (annealed)	69 MPa N_2	993
	69 MPa H_2	724
C1025	69 MPa N_2	730
	69 MPa H_2	552

in contrast, shows the behavior of a material that is not suitable for cryogenic service. In the case of Fig. 11-2, the yield strength increases more rapidly than the tensile strength as the temperature is lowered with the consequence that eventually these two strengths are almost equal, indicating a brittle material. Good materials for cryogenic service include such metals as aluminum alloys, 300 series (austenitic) stainless steels, and copper [1].

If the structural materials are used to contain hydrogen, another type of embrittlement is possible. Although there are three types of hydrogen embrittlement, the type of concern here is termed "environmental hydrogen embrittlement," which can occur by subjecting the equipment to hydrogen, usually at elevated pressure. Table 11-3 shows the consequences of hydrogen action on three different metals resulting in varying degrees of deterioration in their structural strengths. Several mechanisms have been proposed for the effect of hydrogen on metals, and it has been said that if the conditions are sufficiently stringent, hydrogen will affect almost any material.

Tests comparing strain to failure have shown that the magnitude of the effect of hydrogen is a function of temperature and is maximized at temperatures between 200 and 300 K. Thus, one might think that hydrogen embrittlement is not a problem for cryogenic service. However, most cryogenic equipment that will contain hydrogen will see some service at ambient temperature, and large temperature gradients frequently exist in equipment. Therefore, cryogenic materials for service with hydrogen must be chosen to be as resistant to hydrogen as possible. As with metals for cryogenic service, good materials for hydrogen service include aluminum alloys, copper, and stable austenitic stainless steels. In addition, it is important to avoid plastic strain in metals because straining the material in a hydrogen atmosphere promotes the embrittlement of the material [1].

11-4-2 Buildup of Pressure

One of the most commonly encountered hazards of handling cryogenic fluids comes from the unwanted buildup of pressure. That such large pressures can result does not come

Table 11-4 Pressure required to maintain liquid density at room temperature

Substance	Pressure
Nitrogen	296 MPa
Hydrogen	172 MPa
Helium	103 MPa

as a surprise when one considers the large thermal expansion coefficient of the liquids and their very large expansion as evaporation and warming of the gases to ambient temperature occurs (see Table 11-1). However, the pressures that can be obtained by confining a volume of cryogenic liquid are much higher than one might compute by merely considering the volume ratios shown in Table 11-1 and using the ideal gas law to compute a pressure.

As the pressure of a gas is increased sufficiently, the value of PV/RT becomes significantly greater than 1 and continues to increase monotonically as the pressure is increased further [11]. Table 11-4 shows the approximate maximum pressures that can be reached by attempting to maintain liquid density as the temperatures of three common cryogens are raised to ambient temperature. One way to attempt to maintain liquid density of a cryogenic liquid while allowing its temperature to rise to ambient levels is to have a pipe filled with liquid and then close two valves in series. Of course, the pressures would usually not be reached because the pipe walls would rupture before reaching that pressure in most cases.

Cryogenic storage vessels should never be totally filled with liquid, and usually a part of the storage volume above the liquid surface (called ullage) is reserved for the gas. Typical ullage volume is a minimum of 10% of the total volume of the vessel. If a cryogenic storage vessel is closed off and not allowed to vent boil-off gas proportional to the heat leaked into the vessel, the storage pressure will rise and the temperature of the stored fluid will rise with it. The thermal expansion coefficients of the common cryogens are listed in Table 11-5. That they are large can be seen from the comparison with water at its normal boiling point. If the temperature of the liquid rises sufficiently,

Table 11-5 Thermal expansion coefficients of various fluids at the normal boiling point $[1/V(dV/dT)_p]$

Substance	Coefficient
Liquid helium	0.210/K
Liquid hydrogen	0.0164/K
Liquid neon	0.0144/K
Liquid nitrogen	0.0057/K
Liquid argon	0.0044/K
Liquid oxygen	0.0044/K
Water (for comparison)	0.0007/K

the liquid can completely fill the vessel, a situation that is termed "liquid full." At this point a much faster pressure rise rate can be expected, which can lead quickly to the explosion of the vessel.

Another frequently encountered mechanism for a more rapid pressure rise in a closed cryogenic system is that of thermal stratification. The heat that enters the storage volume at the bottom of the vessel will heat the entire volume of contained fluid. However, the heat that enters the sides warms the adjacent liquid, which then travels up along the wall of the vessel until it accumulates at the liquid surface. Because the pressure in the vessel is established by the temperature of the liquid surface, this unequal distribution of incoming energy will cause a pressure rise rate that can be as great as ten times the normal rise rate if all of the incoming heat were to be distributed equally within the entire volume of the liquid (see Fig. 11-3).

In cases where it is necessary to close off a storage volume, some mechanism to prevent thermal stratification is usually provided to preclude the premature venting of the fluid and maintain acceptable pressures within the vessel. Because of the vibration, a

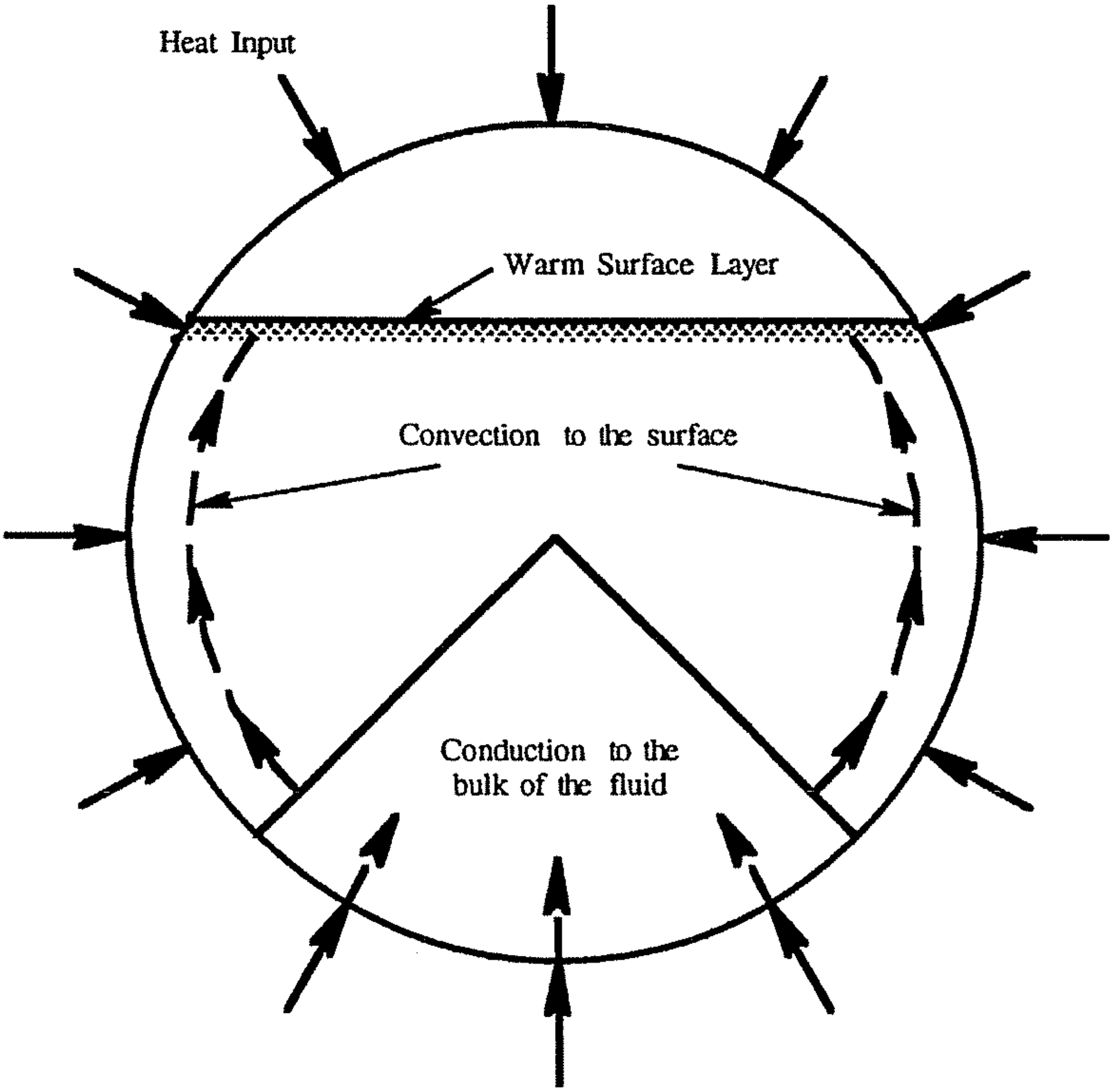

Figure 11-3 Schematic of heat flows into a cryogenic dewar.

highway transport will have a lower pressure rise rate as long as it is driven over the road. When the highway transport is stopped, the pressure rise rate can increase dramatically owing to thermal stratification [1]. Another method to prevent thermal stratification that has been proven effective is the inclusion of thermal shorts of high-thermal-conductivity material, which tend to equalize the temperature between the surface and the lower regions in the storage volume. Even the addition of a noncondensable gas stream at the bottom of the vessel to stir the fluid has been effective in preventing thermal stratification [1].

Because of the potential of unacceptable pressures arising within a cryogenic system it is necessary to provide for pressure relief in case the pressure in the system should start to rise above an acceptable level. There are several types of volumes that require pressure relief. The most obvious of these volumes is that in which the liquid is present, such as a storage volume or cryogen bath. A similar volume is found in a transfer line between two valves that can be closed. A less obvious volume is that containing a gas or condensed liquid in a volume being cooled by an external bath of cryogen or a flowing stream of refrigerant gas.

For the storage of the lower-boiling cryogenic liquids (neon, hydrogen, or helium), an evacuated insulation space is usually necessary for thermal isolation of the cold system. These three liquids are sufficiently cold that if any air were to enter the evacuated insulation system, the air will condense on the cold inner surface of the insulation space and at that temperature will exert essentially zero vapor pressure. Table 11-6 presents some approximate vapor pressures of higher-boiling substances at the temperature of liquid hydrogen and liquid helium. The condensed solid air will, therefore, give no evidence of its presence until the colder liquid being stored is removed. At that time the trapped air can evaporate and exert its full pressure, which can be sufficient to explode the outer vacuum jacket or implode the inner vessel. For this reason pressure relief must also be provided for the vacuum jackets in systems containing the lower-boiling cryogenic liquids.

A standard for pressure relief devices is given by the Compressed Gas Association [12]. In general the relief valves should be sized to allow the maximum flow of

Table 11-6 Vapor pressure of some gases at selected temperatures (Torr)

Vapor	4 K	20 K	77 K	150 K	Triple[a] point temperature
Water	[b]	[b]	[b]	10^{-7}	273
Carbon dioxide	[b]	[b]	10^{-8}	10	217
Argon	[b]	10^{-13}	160	[c]	84
Oxygen	[b]	10^{-13}	150	[c]	54
Nitrogen	[b]	10^{-11}	730	[d]	63
Neon	[b]	30	[d]	[d]	25
Hydrogen	10^{-7}	760	[d]	[d]	14

Note: Estimates; useful for comparison purposes only.

[a] Solid and vapor only at equilibrium below this temperature; no liquid.

[b] Less than 10^{-13} Torr.

[c] Greater than 1 atmosphere.

[d] Above the critical temperature, liquid does not exist.

exiting fluid that can be anticipated at the maximum allowable pressure in the storage volume. Usually a failure of the insulation system (such as a complete loss of vacuum) is considered. Also, in the case of a transport vessel, the possible upset of the vessel should be considered because it might result in the gas vent location being below the liquid surface. In this case it will be necessary to vent a liquid volume sufficient to maintain a safe pressure within the vessel. If the vessel contains a device capable of storing energy, such as a superconducting magnet, the pressure rise caused by the sudden dissipation of the stored energy into the fluid must also be considered.

Another mechanism for increasing the rate of pressure rise in a cryogenic storage volume is that of pressure oscillations. In the case of heating a flowing cryogenic liquid, the possibility and severity of these pressure oscillations depend upon the rate of heat transfer. A correlation describing the onset and severity of these oscillations is available in the literature [1]. For the colder-boiling cryogens, hydrogen and helium, oscillations can be excited by connecting the cold storage volume to ambient temperature by means, for example, of a tube to a pressure gauge. If this problem occurs, a change in the pressure measurement system might be necessary. The important parameters are the ratio of the temperatures at the ends of the tube, the tube diameter, and the temperature gradient along the tube [13].

Table 11-7 shows that the colder the normal boiling point of the cryogen, the more difficult is its handling. As seen in Table 11-7, this increased difficulty occurs because, as the normal boiling point temperature becomes lower, the heat of vaporization per unit volume of liquid also decreases. Added to this is the fact that, as the boiling temperature becomes lower, the difference in temperature (the driving force inducing heat into the cold system) is also increasing.

The storage of LNG presents a special hazard of pressure rise. This has been termed "rollover." Liquefied natural gas is not a single component fluid. Rather, it consists of several constituents, each with a different vapor pressure and a different density at a given temperature. Heat enters the tank both at the sides and the bottom. The liquid at the top can lose heat by evaporation, whereas the bottom can only lose heat by conduction to the top layer. This results in a warmer layer at the bottom, which becomes less dense as its temperature rises. At the same time the top of the liquid becomes heavier as it loses

Table 11-7 Temperature difference and heat of vaporization for various substances

Substance	Normal boiling point (K)	Heat of vaporization (J/cm^3)	Delta T^a (K)
Oxygen	90	243	210
Nitrogen	77	160	223
Neon	27	104	273
Hydrogen	20	32	280
Helium	4	2.5	296
Water^b	373	2255	–

Note: Both temperature difference and heat of vaporization affect pressure rise rate.

[a] Temperature difference from ambient to normal boiling point.

[b] For comparison only.

its lighter components. Eventually the difference in densities can cause a rolling over of the liquid so that the warmer liquid moves to the top, where it will evaporate more rapidly without the pressure of the hydrostatic head above it [14]. The large increase of boil-off vapors can be a hazard because they are combustible.

11-4-3 Condensation of Atmospheric Gases and Higher-Boiling Substances

All cryogens can condense water vapor and carbon dioxide and many other compounds. Table 11-6 shows how low the vapor pressure is for several substances that could be condensed. Liquid nitrogen, liquid hydrogen, and liquid helium (or even the cold vapors from the latter two) can condense oxygen or air. This is likely to occur if these fluids, or cold vapors from these fluids, are passed through an uninsulated pipeline.

In general, the condensate from atmospheric air, condensing on an exposed surface at liquid nitrogen temperature, or colder, is more hazardous than liquid air. The composition of this condensate is about 50% oxygen, and subsequent evaporation can further enrich the oxygen content. Figure 11-4 shows the composition of condensate if air with 21%

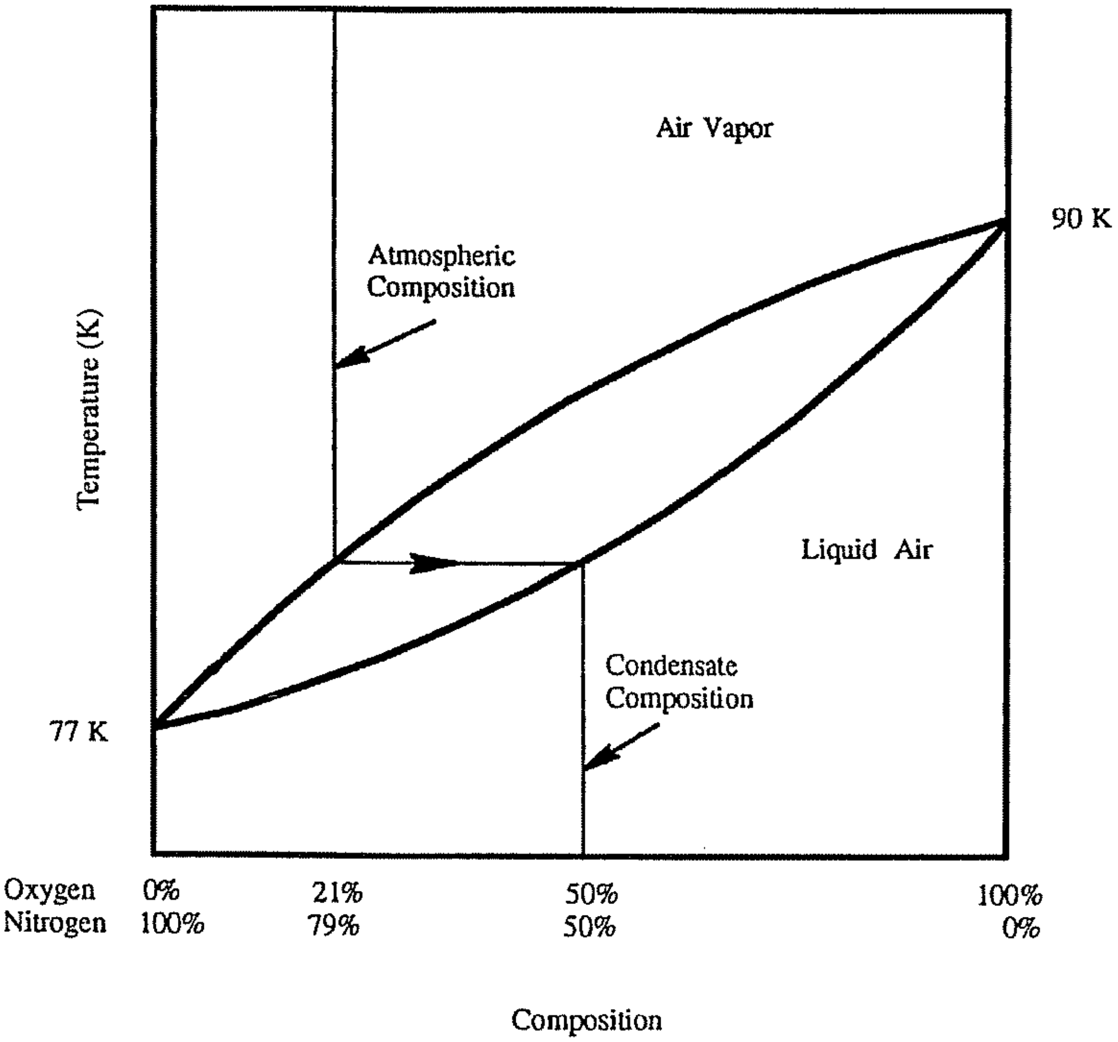

Figure 11-4 Oxygen–nitrogen phase diagram showing ambient and condensate compositions.

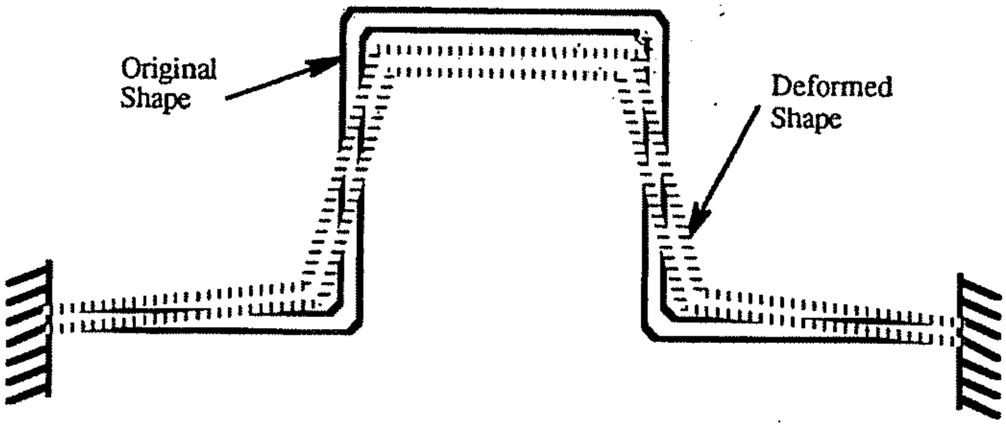

Figure 11-7 Schematic of cryogenic transfer line before and after cooling.

displacements. (Figure 11-7 shows an exaggerated view of the line after cooling to operating temperature.) If stresses are found to be too great, it is necessary to include more or larger "U" bends or elbows. If this is not desirable, flexible piping can be used if the additional pressure drop is not excessive. For vacuum-jacketed lines it may also be necessary to allow for motion of the vacuum jacket by the use of expansion bellows.

The previous considerations are for a case at thermal equilibrium. Thermal transients can give rise to thermal gradients (and stresses) during processes like cooling a piece of equipment from room temperature down to operating temperature. A thick flange can reach liquid hydrogen temperature at the inner surface while still at room temperature at the outer surface. Under these conditions it is also necessary to know something about the temperature gradient to estimate the thermal stress because the stresses can depend upon the shape of the thermal gradient as well as the total temperature difference. Therefore, cooling flow rates must not be too fast, and some maximum permissible cooling flow rates have been calculated by Novak [15].

Cooling a piece of equipment like a long, horizontal transfer line too slowly can result in another type of thermal stress. Usually a transfer line is cooled by introducing a flow of the cryogen through the line when it is initially at ambient temperature. The line is then cooled by evaporation of the cryogen. A snapshot illustration of the line at some time during the cooling process shows that several types of flow can occur within the line. When the line is partially cooled, the initial portion of the line will be filled with liquid. Downstream of this portion is a length that is still not at the temperature of the liquid and therefore is being cooled by heating the liquid and causing some two-phase flow. Even further downstream the liquid has all been evaporated, and the cold gas is precooling the line while the vapor is warming up to close to ambient temperature. If the two-phase flow is stratified flow, it is possible for the bottom of the line to cool faster than the top. This can cause the line to bow upwards and may cause unacceptable thermal stresses. A more detailed discussion of this phenomenon may be found in the literature [1].

11-5 COMBUSTION HAZARDS

Two of the commonly encountered cryogens (hydrogen and LNG) are flammable and can give rise to the hazard of unwanted combustion. In addition, oxygen is a strong promoter of combustion and can present a similar hazard. Although this latter hazard is more obvious in the case of pure oxygen, liquid air is also hazardous, and, as pointed out in section 11-4-3, air condensing from the normal atmosphere can have an oxygen concentration of up to 50% (see Fig. 11-4) and is even more hazardous than liquid air.

11-5-1 Fuels (Hydrogen and LNG)

Three ingredients are needed for combustion to occur. These are a fuel, an oxidizer, and an ignition source. Safety of operation requires that, wherever possible, the attempt should be made to eliminate two of these three at a given location. Consequently, every effort must be made to eliminate ignition sources. Ignition sources include such obvious things as open flames, smoking, and welding. Less obvious and more difficult to control ignition sources include static electricity, sparking devices, high-velocity impact of solid particles, heat of rapid compression, and friction. The elimination of these ignition sources requires precautions such as using approved electrical devices, assuring the absence of unwanted solid particles within the system, properly designing equipment, and properly operating the system [1].

Combustible mixtures must also be avoided. This effort involves complete purging of residual air from the system before introducing the combustible cryogen. In the case of hydrogen, everything other than helium can be condensed to a solid at the temperature of the liquid hydrogen. This results in another reason for complete purging because, even if not combustible, such particles can cause erosion of valve seats or can block access to relief valve ports.

Flammable substances are ignitable within a range of composition that is dependent upon temperature and pressure of the mixture. Combustion can be a reaction of fuel and oxidizer that is controlled by heat transfer from the burning substances into the adjacent combustible mixture, heating it to its ignition temperature. This combustion reaction is called "deflagration." A more vigorous reaction occurs if the combustible mixture is heated to the ignition temperature by a shock wave. This is termed "detonation." Although either of these reactions presents a definite hazard, detonation is generally much more serious. Concentration ranges of combustibility and detonability can be found in the literature [1,16,17].

11-5-2 Oxidizers

Oxygen is sufficiently reactive that almost anything that is not already completely oxidized can be made to burn if the right conditions exist. Stainless steel has been known to burn in the presence of liquid oxygen. Consequently, in the handling of oxygen, two of the three ingredients necessary for combustion (fuel and oxidizer) are almost always present. This fact makes even more important the elimination of ignition sources, including all of those mentioned above.

Liquid air (21% oxygen) and air condensed from the atmosphere are also hazardous substances, but, as the oxygen content is increased, the mixture becomes even more hazardous. Figure 11-8 illustrates the increase in reactivity of a substance as the oxygen concentration is increased. In this case an adhesive (HT-424) is used as an illustration.

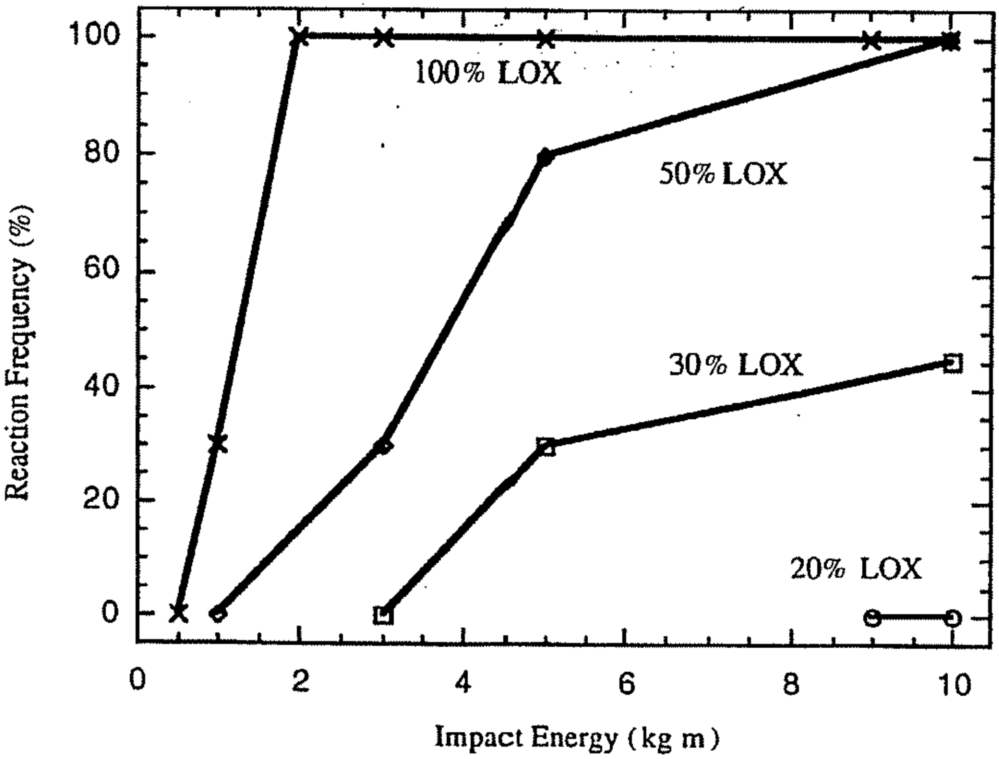

Figure 11-8 Effect of liquid oxygen (LOX) concentration on reaction of HT-424 adhesive.

However, similar behavior is obtained with many materials. The data shown are for tests in which a variable mass is dropped on a striker pin attached to the specimen, which is immersed in the liquid oxygen–nitrogen mixture. From the number of ignitions, as shown in Fig. 11-8, it can be seen that, although a 50% oxygen mixture is not as reactive as 100% oxygen, it still is much more reactive than true liquid air (21% oxygen) [18].

Safety in working with oxygen requires the proper selection of materials and scrupulous cleanliness. Materials with high ignition temperatures, high specific heats, high thermal conductivity, and low heats of reaction are desirable [1,19]. Cleanliness is important because most impurities will have lower ignition temperatures. If the impurities ignite, this combustion can subsequently ignite materials that otherwise would not have been ignited. Several cleaning methods and cleaning agents are recommended [1,20].

11-6 REGULATIONS, STANDARDS, AND GUIDELINES

There are three types of safety documents. Regulations are enacted by governmental bodies and have the force of law. Standards (also known as codes) are usually issued by associations with a wide range of members as a means of ensuring that common safety interests are met in a uniform and predictable manner. Standards are typically thought of as representing the consensus of technical experts on the subject at hand. Guidelines are developed by organizations based on their specific needs. The three types of documents are not mutually exclusive. Regulations frequently incorporate standards, either directly or by reference, thus giving them the force of law. Standards often refer to other standards or regulations to avoid repetition and to reduce inconsistencies, which can develop when differing groups cover the same subject matter. Guidelines can require members or employees of their organization to follow standards and frequently cite relevant regulations and standards to ensure they are applied when appropriate.

There are usually several levels at which governmental regulations can be established. These range from cities or counties at the local level, to states or provinces at the regional level, and to the federal or national government at the highest level. In the United States, for example, national regulations are found in the Code of Federal Regulations (CFR). The two titles most relevant to cryogenics are Title 29, Labor, which covers occupational safety and health and Title 49, Transportation, which covers the transportation of hazardous materials. In addition, groups of nations can develop consistent standards through organizations such as the International Standards Organization (ISO) and then incorporate these standards into regulations or treaties.

In addition to the ISO, many nations have their own standards organizations. It is not possible to list them all here, but representative associations in the United States include the following: American Society of Mechanical Engineers (ASME), American National Standards Institute (ANSI), American Society for Testing and Materials (ASTM), National Fire Protection Association (NFPA), Factory Mutual Engineering and Research (FM), and the Compresssed Gas Association (CGA). In addition to their safety value, many of these standards provide useful design information.

Guidelines are developed by companies, laboratories, and universities to address the specific needs of each organization. They are frequently available upon request and can provide valuable information and advice. All of the above documents can change with time, and thus one must be aware of the latest developments to ensure that current safety documents are followed.

11-7 CONCLUSIONS

At this point it should be clear that safety is a philosophy that must be integrated into all aspects of any cryogenic project. It is not an afterthought that can be adequately addressed after a system has been designed or built. Consideration of safety should begin at the conceptual design phase and continue through final design, procurement of equipment, fabrication, and assembly. Careful consideration at the conceptual design phase can often eliminate problems that will require complicated and expensive corrections if addressed later.

Safety is not finished when a project becomes operational. Operation requires planning, which includes established standard operating procedures and written checklists as well as previously thought-out responses to unexpected behavior of systems and emergencies (contingency checklists). It is important to avoid modifying any system without examining all of the possible consequences. Many accidents are caused by the unexpected consequences of quick repairs instituted without a thorough understanding of all aspects of system operation.

Finally, training of personnel should be a continuing effort and should not merely be passed from one employee to the next without some referral back to the fundamental safety requirements of the system. Without structured training of new personnel there is no way to be sure that all hazards are identified and all safety issues are adequately addressed.

REFERENCES

1. Edeskuty, F. J., and Stewart, W. F., *Safety in the Handling of Cryogenic Fluids* (New York: Plenum Press, 1996).
2. Gonzalez, F., and Walton, R. L., "Cold-Induced Tissue Injuries," Chap. 199 in *The Clinical Practice of Emergency Medicine*, A. Harwood-Nuss, C. H. Linden, R. C. Luten, G. Sternbach, and A. B. Wolfson, eds. (Philadelphia: J. B. Lippincott Co., 1991).
3. Klainer, P., "Hypothermia," Chap. 200 in *The Clinical Practice of Emergency Medicine*, A. Harwood-Nuss, C. H. Linden, R. C. Luten, G. Sternbach, and A. B. Wolfson, eds. (Philadelphia: J. B. Lippincott Co., 1991).
4. *Oxygen Deficient Atmospheres (less than 19.5%)*, Compressed Gas Association Bulletin CGA SB-2 (Arlington, Varginia: Compressed Gas Association, 1992).
5. *Carbon Dioxide*, Compressed Gas Association Bulletin CGA G-6 (Arlington, Virginia: Compressed Gas Association, 1984).
6. *Safe Handling of Liquid Carbon Monoxide*, Compressed Gas Association Bulletin CGA-P-13 (Arlington, Virginia: Compressed Gas Association, 1989).
7. American Conference of Government Industrial Hygienists Technical Information Office (Glenway Ave. Bldg. D-7, Cincinnati, OH 45211, 1993).
8. *1992–1993 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices* (Cincinnati, Ohio: American Conference of Governmental Industrial Hygienists, 1992).
9. Gatwood, G. T., and Murphy, G. F., "Safety in the Chemical Laboratory: Ozone Hazards," *J. Chem. Ed.* 46, 1969):A103–A105.
10. Zabetakis, M. G., *Safety with Cryogenic Fluids* (New York: Plenum Press, 1967).
11. Dodge, B. F., *Chemical Engineering Thermodynamics* (New York: McGraw–Hill, 1944).
12. "Pressure Relief Device Standards, Part 2—Cargo and Portable Tanks for Compressed Gases," CGA S-1.2 (Arlington, VA: Compressed Gas Association, 1994).
13. Gu, Y., and Timmerhaus, K. D., "Experimental Verification of Stability Characteristics for Thermal Acoustic Oscillations in a Liquid Helium System," *Adv. Cryog. Eng.* 39B (1994):1733–1740.
14. Johnson, P. C., "Liquefied Natural Gas," Chap. 3 in *Liquid Cryogens*, vol. II, K. D. Williamson, Jr., and F. J. Edeskuty, eds. (Boca Raton, Florida: CRC Press, 1983).
15. Novak, J. K., "Cool-down Flow Rate Limits Imposed by Thermal Stresses in Liquid Hydrogen or Nitrogen Pipelines," *Adv. Cryog. Eng.* 15 (1970):346–353.
16. Coward, H. F., and Jones, G. W., *Limits of Flammability of Gases and Vapors*, U.S. Bureau of Mines Bulletin 503 (Washington, D.C.: U.S. Government Printing Office, 1952).
17. Zabetakis, M. G., *Flammable Characteristics of Combustible Gases and Vapors*, U.S. Bureau of Mines Bulletin 627 (Washington, D.C.: U.S. Government Printing Office, 1965).
18. Key, C. F., *Compatibility of Materials with Liquid Oxygen*, vol. 1, NASA Technical Memorandum, NASA TM X-64711 (Alabama: George C. Marshall Space Flight Center, October 1972).
19. Schmidt, H. W., and Forney, D. E., *ASRDI Oxygen Technology Survey*, vol. IX, *Oxygen Systems Engineering Review*, NASA Report SP-3090 (Springfield, Virginia: National Technical Information Service, 1975).
20. "Cleaning Equipment for Oxygen Service," CGA G-4.1 (Arlington VA: Compressed Gas Association, 1985).