

*Keynote Paper*

## **CRYOGENICS: ITS PRODUCTION, PROPERTIES AND INDUSTRIAL APPLICATIONS**

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**Abstract** Cryogenics is the science and technology that relates to the temperature zone from 123 Kelvin ( $-150^{\circ}$  C) down to near zero Kelvin. Many technologies, that are already matured, and many more, that are still growing, rely on working at such low temperatures. During the last 125 years (1877 is called the birth-year of cryogenics when Louis Paul Cailletet of France and Raoul Pictet of Switzerland produced a small amount of liquid oxygen), there has been relentless effort to utilize this technology to almost all conceivable fields. In this paper, we have briefly touched the major aspects of this technology, including methods of production of low temperatures, their applications in various fields and special properties of cryogenics and solids at low temperature that differentiate their applications at cryogenic temperatures from those at ambient or high temperatures. Applications in various fields of engineering have been discussed. Safety aspects involved with handling cryogenics have been highlighted.

*Keywords: Cryogenics, Cryorefrigerator, Cryogenics, Superconductivity*

### **INTRODUCTION**

From the seventeenth century, physicists and physical chemists have been studying the physical properties of gases from high pressure high temperature state down to low temperature low pressure state. They found that, unlike many other fluids, their properties could not be determined in all the states because some of the gases like Air, O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub> and Helium are not available in liquid (and solid) state. Evolution of thermodynamics in the late eighteenth century was offering a better understanding of the relationships between heat and work and the laws of thermodynamics finally made it possible to achieve a temperature below that of the environment and the science of refrigeration was born. The first vapor compression refrigerator was made at about the middle of nineteenth century and by 1880 ice making machines were available in the market. The brewers and the butchers were the initial sponsors of such machines. The stage thus was set for the advent of cryogenics, the science and technology of deep low temperature.

### **DOMAIN OF CRYOGENICS**

One of the ways of achieving a temperature of less than 123 K is by liquefaction of so-called permanent gases like O<sub>2</sub> (90.18 K), N<sub>2</sub> (77.35 K), Air (78.9 K), Argon (87.28 K), Neon (27.09 K), Hydrogen (20.27 K),

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Helium (4.22 K) etc. Their boiling points at atmospheric pressure are given in parenthesis. There are primarily two uses of cryogenics: use of cold and use of pure gases.

#### **1. Use of Cold**

During the last one hundred years, there have been continuous efforts to use cryogenic temperatures for the increase of production, improvement of quality of products and reduction of cost of production. The cold can be produced and used in two ways:

**Production of cold by a cryorefrigerator** The product, sample or the substance to be cooled is placed on a surface that is cooled to cryogenic temperatures. It is analogous to a household refrigerator, where the user does not care how the refrigerator cold chamber is cooled, as long as it gives the desired temperature at a given capacity. A cryorefrigerator coldhead may be cooled by a closed cycle system that works on one of the many thermodynamic cycles available for the purpose. The choice of the cycle depends on many factors, like, reliability, cost of equipment, cost of production, size, weight, vibration etc. A cryorefrigerator is usually tabletop equipment though it can be scaled up or down to a great extent depending on its applications. The temperature range of the cryorefrigerators is from 100 K to microkelvin and the range of capacity is from a few hundred watt to one milliwatt. Of course, different types of cryorefrigerators

are employed to attain different combinations of temperatures and capacities.

The working fluid, that flows around in a cyclic process inside the system, is usually nitrogen or helium (analogous to Freon-12, Freon 134a, Freon 22 or ammonia in household refrigerators or window airconditioners), and it is not necessary that they have to be liquefied at any stage. The working fluid remains mostly in the gaseous state while exchanging heat with the cold surface that serves as the barrier between the gas and the sample. Electrical energy is the only input required in such applications.

**Use of cryogenic liquids** Cryogenic liquids, which have very low boiling points, may be poured over a substance for cooling it to cryogenic temperature. The target temperature would decide which liquid is to be used. If, for example, 25 Kelvin is the target temperature, hydrogen or helium should be used. Though, thermodynamically speaking, liquid hydrogen is the better choice in this case, it is often excluded because of its combustible character and the neutral liquid helium is preferred. Though the use of liquid cryogenics (as the family of cryogenic fluids is called) makes the cooling faster and more effective, it may be avoided under circumstances where cryogenic liquid replenishment is impossible or it is difficult to handle. Cryogenic liquid is the only input required in such application.

Cryogenic liquids are usually produced in large tonnage plants, though they may also be produced in small liquefiers based on closed cycle cryorefrigerators. It is called a "cold vector", because its cold may be used at a faraway location from its source of production. Liquid hydrogen, which is thought to be the future source of energy, can also be transported to a distant location and is rightly called the energy vector.

## 2. Use of Pure Gases

Gases, liquids and solids have got many useful industrial applications in their pure forms. Unfortunately, however, they are available in nature only in the form of mixtures. Sometimes a mixture may contain more than one useful component, when one has to do "separation" to get the pure fluids. Sometimes a useful component is mixed with impurities, when it needs to be "purified".

Of the cryogenic fluids, O<sub>2</sub>, N<sub>2</sub>, argon, neon, krypton and xenon – the so-called "permanent gases" – are available as mixtures in air. H<sub>2</sub> is produced by dissociating water or from other industrial processes. Helium is available in nature mixed with natural gas.

Usually the processes of distillation, adsorption and membrane separation are used for separating the gases. Out of these three processes, the process of distillation, which gives products in large quantity and with high purity, involves partial liquefaction of the feed gas. Since the liquefaction temperature of these gases lie within the range of cryogenics, the distillation process involving these gases are called cryogenic distillation.

## PRODUCTION OF CRYOGENIC TEMPERATURES

Production of cryogenic temperatures is accomplished in two ways: 1. Creation of cold at the coldhead by means of closed-cycle cryorefrigerator, and 2. Liquefaction of gases.

### 1. Closed Cycle Cryorefrigerator

A closed cycle cryorefrigerator is analogous to a household refrigerator. In a household refrigerator, cold is produced in the cold chamber and the working fluid Freon flows in close cycle inside the machine. In a cryorefrigerator, in an analogous manner, cryogenic temperature is produced in the coldhead, while helium gas flows in close cycle inside the machine. A household refrigerator, which is shown in Fig 1(a) in a schematic diagram, works on a thermodynamic cycle called "vapour compression cycle" and can achieve a lowest temperature of  $-80^{\circ}\text{C}$  (193 K) in multiple stages. On a single stage, usually, one can get a temperature  $10^{\circ}\text{C}$  (air conditioners),  $-5^{\circ}\text{C}$  (household refrigerators),  $-10^{\circ}\text{C}$  (bottle coolers) etc. depending on the suction pressure employed. A close cycle cryorefrigerator, however, may work on many thermodynamic cycles, whose choice depends on various factors like the cost of equipment, power consumption, size, weight, vibration, reliability etc that is demanded from the machine depending on its application. A Gifford-McMahon cryorefrigerator, shown in Fig 1(b), for example, offers the advantage of low cost, reliable operation for uninterrupted 10,000 hours at least and achieves a temperature of 5 Kelvin at the lowest (usually 15 to 20 Kelvin) in a two-stage machine. Since it is not possible to repair or maintain a cryorefrigerator in a satellite (where it is used to cool the electronic sensors) within its expected life span of 10 years, high reliability of operation is needed. The power consumption and weight also has to be smaller. These demands are met by integral Stirling cooler, which is shown schematically in Fig 1(c). A submarine moving deep below the ocean can be detected by a superconducting device called SQUID, which is borne in a helicopter and this SQUID has to be cooled to a cryogenic temperature at 10 Kelvin.

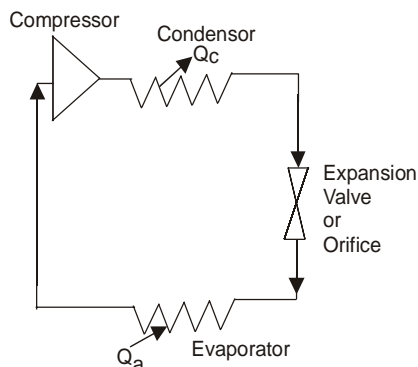


Fig 1(a) :A single stage vapor compression refrigeration

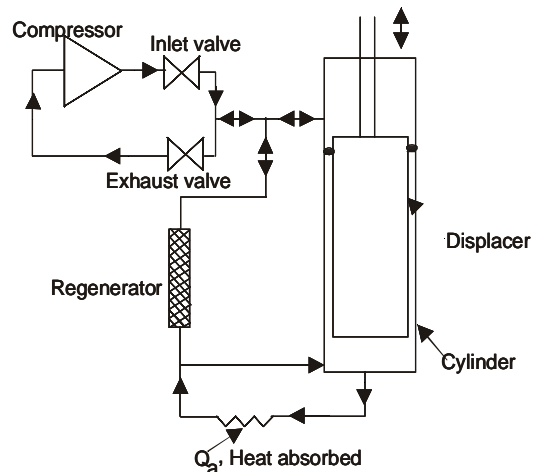


Fig 1(b): A single stage Gifford McMahon Cryorefrigerator

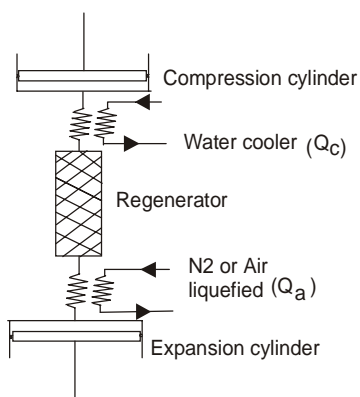


Fig 1(c): An integral Stirling cycle cryocooler

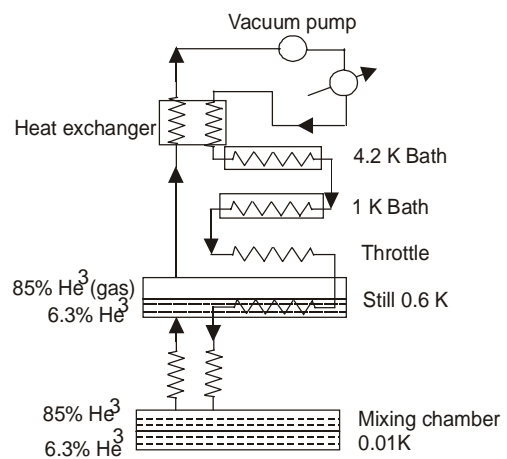


Fig 1(e): He<sup>3</sup>-He<sup>4</sup> Dilution Refrigerator

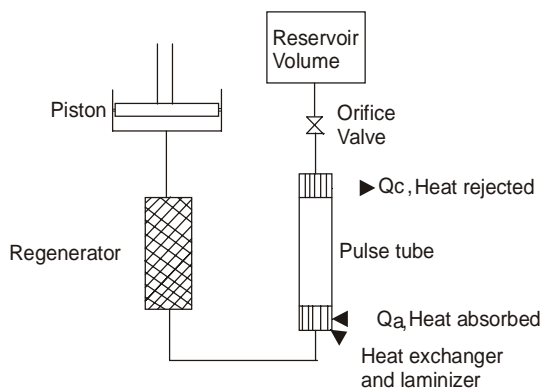


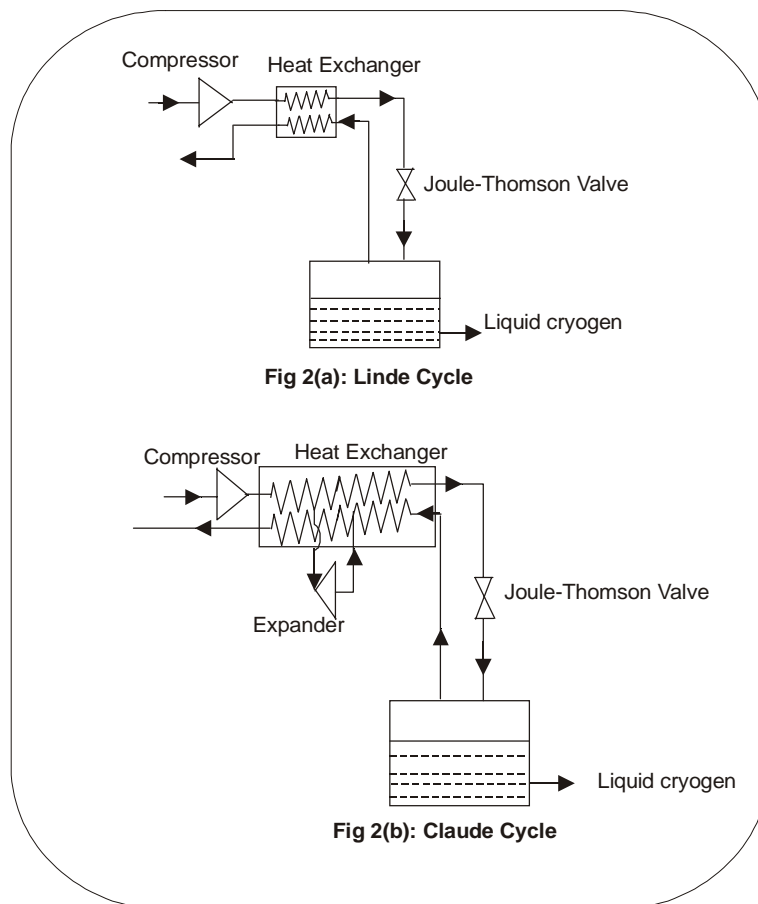
Fig 1(d): An orifice pulse tube refrigerator

The coldhead, however, has to be absolutely free of vibration and this criterion can be met by a Pulse Tube cryorefrigerator, as shown in Fig 1(d). A temperature of about 15 K can be achieved in a He<sup>3</sup>-He<sup>4</sup> Dilution refrigerator, as shown in Fig 1(e). Thus, it can be seen that depending on the criteria of applications and the temperature levels, different cycles of cryorefrigeration are used.

## 2. Liquefaction of Gases

At atmospheric pressure ammonia and Freon-12 boil at

-33°C and -30°C respectively. At pressures above or below atmospheric pressure, the corresponding boiling points increases or decreases. It means that when ammonia or Freon-12 are brought in direct or indirect contact with any material, the latter is cooled to the corresponding temperatures and hence, the former are



called refrigerants. Ammonia and Freon-12 are available as vapors at ambient temperatures and pressures and when pressurized at about 15 bar(a) and 10 bar(a) respectively and cooled to ambient temperatures, they are liquefied. This is possible because the critical temperatures of these gases are above ambient temperatures. This high pressure liquid, when expanded to a lower pressure, produces a low temperature and we get refrigeration, which in the context of this paper, would better be called as conventional refrigeration.

In order to achieve a temperature below  $-150^{\circ}\text{C}$  (123 K), which is accepted as the borderline between conventional refrigeration and cryogenic refrigeration, some of the gases like  $\text{N}_2$ ,  $\text{O}_2$ , Ar,  $\text{H}_2$  and He need to be liquefied. Since their critical temperatures lie much below the ambient temperature ( $\text{N}_2$  : 126.1 K,  $\text{O}_2$  : 154.6 K, Ar : 150.7 K,  $\text{H}_2$  : 33.2 K and He : 5.2 K), any amount of pressurization and subsequent cooling fails to liquefy them. A novel approach was needed to accomplish the job and the liquefaction of oxygen in 1887 marked the advent of cryogenics. The thermodynamic cycle adopted is called Linde Cycle (after Carl von Linde), as shown in Fig 2(a), which was later improved by Georges Claude in 1902 by adding expansion engine and reducing the working pressure, called Claude Cycle, as shown in Fig 2(b). With the liquefaction of helium by Heike Kamerlingh Onnes in

1908, attaining the lowest temperatures became a reality.

### Production of Pure Gases

Gases appear as mixtures in nature. They can be separated into their pure components by the process of distillation, which requires the presence of both liquid and vapour inside the column. Once air was liquefied, its constituents  $\text{O}_2$  and  $\text{N}_2$  were separated in Linde Single Column (oxygen and nitrogen separately) (Fig 3(a) and 3(b)) and Linde Double Column (oxygen and nitrogen together) (Fig 3(c)). Argon and Neon were recovered in Argon Separation and Purification column and Neon Separation and Purification system. Helium is separated from helium-rich natural gas by distillation process only. A modern air separation plant, separating  $\text{O}_2$ ,  $\text{N}_2$  and Ar, is shown in Fig 4.

### PROPERTIES OF CRYOGENIC FLUIDS

It is important to know the properties of cryogenic liquids and gases in order to use them effectively and safely for the purpose of production, storage, handling, transport and cooling materials. When liquefying nitrogen, it is important to know the enthalpies of gaseous nitrogen at room temperature and of liquid nitrogen at its boiling point in order to determine the amount of cooling necessary to accomplish the task. While storing normal hydrogen in an insulated vessel,

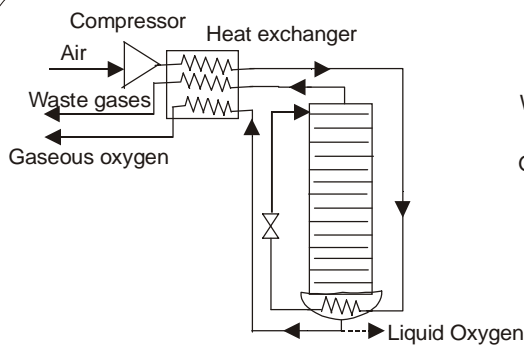


Fig 3(a): Linde single column producing oxygen

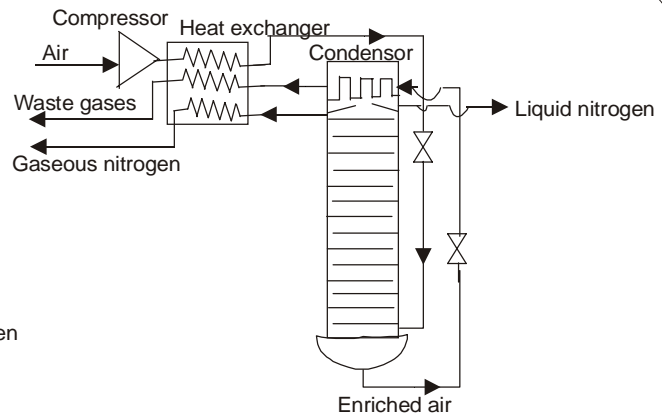


Fig 3(b): Linde single column producing nitrogen

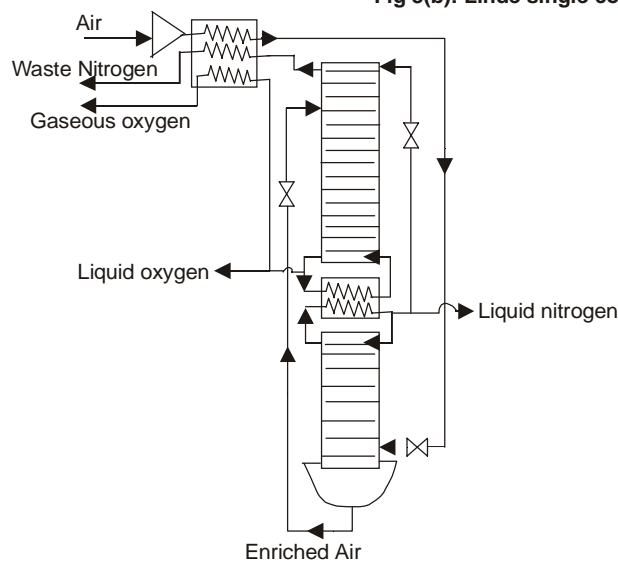


Fig 3(c): Linde Double Column producing Oxygen and Nitrogen

one has to know the property of “ortho-to-para” conversion in liquid hydrogen to estimate its evaporation during storage. The difference of specific volumes at saturated liquid and saturated vapour indicates the pressure to be reached in a confined volume with evaporation of cryogenic liquid and thus avoid a potential explosion. Some of the important properties of cryogenic fluids are given in Table 1.

### Special Properties of Hydrogen

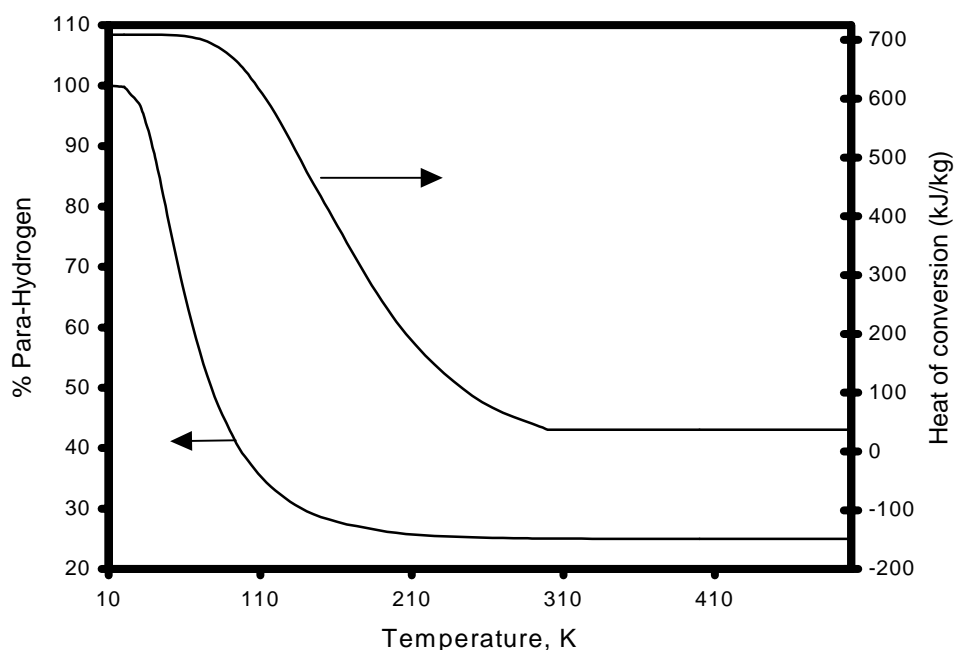
**Ortho-to-para conversion** Hydrogen can exist in two different molecular forms: orthohydrogen ( $o\text{-H}_2$ ) and parahydrogen ( $p\text{-H}_2$ ). Hydrogen at ortho state is at a higher energy level in which the protons in the two nuclei spin in the same direction, while in lower energy para state the protons spin in opposite direction. At ambient and higher temperature, hydrogen consists of 25% para and 75% ortho, which is called “normal hydrogen”. At the normal boiling point of liquid hydrogen, equilibrium shifts to almost

100% para hydrogen. Conversion from ortho to para is exothermic and the heat of conversion increases with decreasing temperature, such that at 20 K it is 702 kJ/kg, which is higher than the latent heat of liquid hydrogen 443 kJ/kg. Consequently, liquid normal hydrogen would completely boil-off on its own, even if it is kept in a highly insulated storage vessel. It is therefore necessary to remove the heat of conversion before it is liquefied and it is thermodynamically more efficient if this removal takes place at higher temperatures, where ortho-to-para conversion occurs simultaneously with cooling so that the hydrogen cooling path closely follows the equilibrium curve. Continuous conversion is, however, very expensive and therefore, it is done at several temperatures in stages starting from liquid nitrogen temperatures in presence of catalysts like, an iron oxide catalyst or a nickel silicate catalyst. Figure 5 shows the equilibrium concentration of para hydrogen and heat of conversion as function of temperature.



**Table 1: Important properties of cryogenic fluids**

Fluid →	Oxygen	Argon	Nitrogen	Air	Neon	Hydrogen	Helium-4
Properties							
Molecular Weight	32.0	39.944	28.016	28.9	20.183	2.016	4.003
Boiling Point, K	90.2	87.3	77.3	78.8	27.2	20.4	4.2
Melting Point, K	54.4	83.2	63.1		24.6	14.0	4.2 at 140 atm
Liquid Density at B.P., kg/litre	1.14	1.4	0.808	0.874	1.205	0.071	0.125
Vapor Density at B.P., kg/m <sup>3</sup>	4.75	5.93	4.415	4.44	9.5	1.286	17.0
Gas Density at 0°C 1 atm(a), kg/m <sup>3</sup>	1.43	1.78	1.25	1.29	0.90	0.09	0.18
Latent Heat of Vaporization at B.P., kJ/kg	213	162	198	205	86	443	21
Viscosity, μ Pa-s	190	252	158	168	130	13.2	3.56
Specific Heat, kJ/kg-K	1.695	1.136	2.05	1.96	1.83	9.68	4.48
Critical Temperature, K	155	151	126	133	44	33	5.2
Critical Pressure. atm(a)	51	49	34	39	27	13	2.3



**Fig 5: Equilibrium concentration of Para Hydrogen and Heat of conversion as function of temperature**

**Hydrogen-Deuterium separation** Hydrogen has an isotope called deuterium, which consists of one proton and one neutron in the atomic nucleus and one orbiting electron. With combination with oxygen, deuterium forms heavy water, which is chemically the same as

regular (light) water, but with the two hydrogen atoms (as in H<sub>2</sub>O) replaced with deuterium atoms (hence the symbol D<sub>2</sub>O). It is the extra neutron that makes heavy water "heavy", about 10% heavier in fact. Equilibrium deuterium (at 20.39 K) contains 97.8% ortho-deuterium

and its boiling point is 23.53 K, while equilibrium hydrogen (0.21% ortho-hydrogen) has a boiling point of 20.27 K.

Heavy water is essential to the operation of nuclear power reactors, where it is used as both a moderator and a heat transfer agent. The function of the moderator is to slow down the emitted neutrons, which increases the fission reaction rate, thus enabling a sustained chain reaction. Ordinary water is also a good moderator, but it absorbs neutrons, which is why light water reactors must use enriched fuel. The use of D<sub>2</sub>O makes it possible to use non-enriched natural uranium.

Cryogenic distillation makes it possible to separate deuterium from natural hydrogen, which contains about 0.015 percent deuterium. The deuterium occurs in the form of HD instead of D<sub>2</sub> and the HD must first be concentrated and converted before the deuterium can be separated from the hydrogen.

### Special Properties of Helium

**Superfluidity** Apart from the common isotope of helium-4, there exists a very rare isotope helium-3. Helium-4 atom consists of two electrons orbiting a nucleus of two protons and two neutrons, while helium-3 has one neutron less. Ordinary helium gas contains about  $1.3 \times 10^{-4}$  % He<sup>3</sup>, so that when we speak of helium or liquid helium, we mean He<sup>4</sup>, whose boiling point at atmospheric pressure is 4.2 K.

Fig 6(a) shows the phase diagram of a normal fluid, which shows that three phases, solid, liquid, and vapor are separated by the melting (fusion), vaporization and sublimation curves. The fusion curve normally has a positive slope, except for a few substances, like water. The terminal point C is called the critical point, above which no clear distinction can be drawn between what is called liquid and what is called gas. There is a solid-liquid-vapor coexistence point, called triple point.

The helium phase diagram shown in Fig 6(b) exhibits many of the characteristics displayed by normal fluids. However, there are some notable differences. Helium has no triple point. There is no temperature and pressure at which the solid, liquid and vapor exist in equilibrium. Helium can never be solidified at atmospheric pressure merely by reducing its temperature. It is necessary to subject it to a pressure above 25 atmosphere.

Helium exhibits striking properties at temperatures below 2.17 K. As the liquid, called Helium I, is cooled, instead of solidifying it changes to a new liquid phase in the neighborhood of 2 K, called He II. The phase transition between the two liquid phases is called lambda ( $\lambda$ ) line, and the intersection of the latter with the vapor pressure curve is known as the lambda point.

Liquid helium I has a thermal conductivity of 0.024 W/mK, while that of liquid He II is 86,500 W/mK. Compare thermal conductivity of copper as 400 W/mK, of stainless steel as 12 W/mK, of plastics 0.2 W/mK and of air as 0.026 W/mK. When a container of liquid He I is pumped to reduce the pressure above the liquid, the fluid boils vigorously as the pressure and the temperature decreases. As the temperature decreases below the  $\lambda$ -point and the fluid turns to become He II, all apparent boiling suddenly stops. High thermal conductivity of liquid He II transports the heat so rapidly that there is no scope even to form the bubble.

The liquid becomes clear and quite, although it is vaporizing quite rapidly at the surface. Liquid He II is also called superfluid, because its viscosity ( $\sim 10^{-12}$  Pa·s) is much lower compared to that of normal liquid helium ( $3 \times 10^{-6}$  Pa·s). Below the  $\lambda$ -point, however, all of He II does not consist of superfluid helium and as the temperature is lowered, the superfluid content increases. Below about 1.1 K, all of liquid He II consists of superfluid helium. Superfluid can enter very thin channels ( $\sim 10^{-5}$  cm) without any loss of pressure or concern of the length of channel. This property is used to cool superconducting magnets.

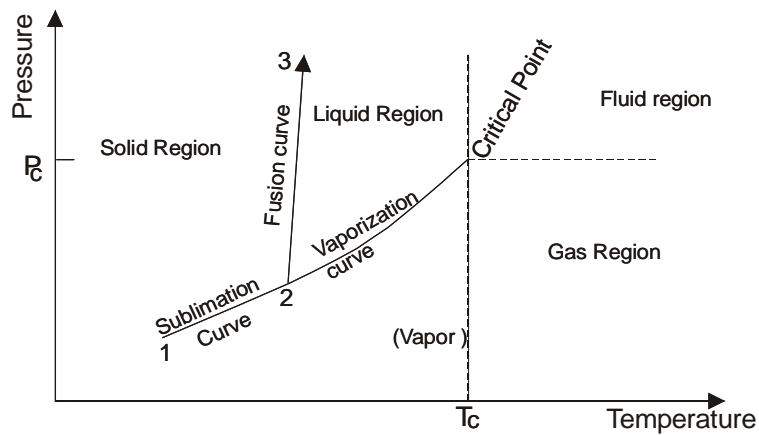
**Separation of helium-3** The isotope helium-3 is very rare and in its liquid form is a clear colorless substance having a normal boiling point of 3.19 K and a density at the normal boiling point of 59 kg/m<sup>3</sup>. The latent heat is 8.5 kJ/kg. Liquid helium-3 in equilibrium with its vapor at a given pressure is significantly colder than liquid helium-4 at the same pressure. In an ordinary dewar system, it is difficult to reduce the helium vapor pressure to less than a corresponding temperature of 0.8 K. With the same system, a temperature of 0.3 K can be achieved with liquid helium-3. This apparent small decrease of 0.5 K should be viewed as 63% reduction in temperature.

Helium-3 and helium-4 are not completely miscible at very low temperature and, in fact, at absolute zero helium-3 is completely insoluble in helium-4. At other temperatures, a phase separation occurs in any mixture of helium-3 and helium-4. This separation into two liquid phases, and the difference in vapor pressures, forms the basis for He<sup>3</sup>-He<sup>4</sup> dilution refrigerator used to obtain temperatures of about 0.15 K.

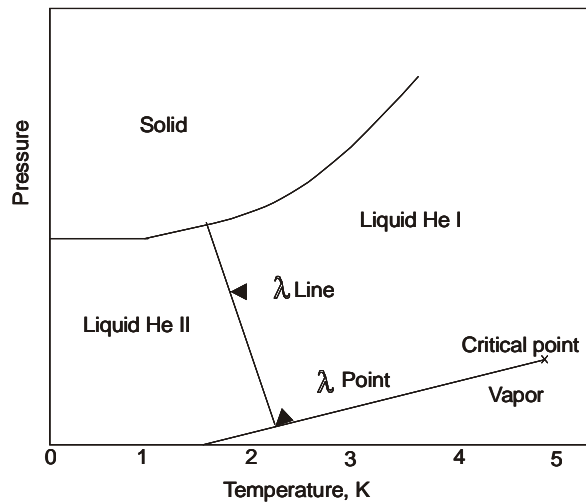
### MECHANICAL PROPERTIES OF SOLIDS

Pure metals and alloys with face centered cubic structures are particularly suitable for use at cryogenic temperatures as many of their properties improves as the temperature falls. Copper and its alloys, aluminium and its alloys, nickel based alloys like Hastalloys, Inconel, Monel, austenitic stainless steels





**Fig 6(a): Pressure-Temperature diagram of a pure substance**



**Fig 6(b): Pressure-Temperature diagram of Helium**

that contain more than 7% nickel are some of the fcc metals that are suitable for cryogenic service. In contrast, body centered cubic metals are more limited in use as most of them undergo ductile to brittle transition at low temperatures. Iron, carbon, Plain carbon steel, low alloy steel, low nickel steel, molybdenum and niobium are bcc metals that become brittle at low temperatures. Many of the hexagonal close packed metals, like zinc, becomes brittle below room temperature, while some, like zirconium and pure titanium, remain ductile down to 4 K. All plastics become brittle at low temperature, except PTFE (well-known in trade name “teflon”), which remains ductile even at 4 K

In general, ultimate stress, yield stress, Young’s modulus and fatigue strength of the important engineering materials including teflon increases with the fall of temperature. Therefore, from these considerations, cryogenic temperatures do not pose any additional problems.

One must have detailed and accurate data on engineering materials at room temperatures down to cryogenic temperatures for selecting proper materials for designing equipment like cryogenic storage and transport tanks, cryogen transport pipelines and other structural and mechanical applications that are subjected to cryogenic temperatures.

### Transport Properties of Solids

**Specific heat** Debye made some major contribution in the theory of heat capacity of solids at low temperature and found that the specific heat capacity depends only on a mathematical function of the ratio of the Debye characteristic temperature  $\theta_D$  to the absolute temperature. This function, called Debye function, is the same for all materials; only  $\theta_D$ , which is a constant characteristic of the material, changes from material to material. It can be seen from Fig 7 that at a temperature equal to  $\theta_D$  and lower, the specific heat of any material falls rapidly from its asymptotic value of  $3R$ . Copper has a  $\theta_D$  of 310 K, aluminium 385 K and lead 85 K, which means that lead retains its specific heat even at a lower temperature and is a much preferred material for constituting the matrix of a low temperature regenerator.

**Thermal expansion (and contraction)** Thermal contraction is an important property for designing any equipment that may be subjected to cryogenic temperatures. Appropriate precaution need to be taken to avoid generation of stresses at the fixed ends or at the interface of joints of dissimilar materials, where the limit of allowable stresses may be exceeded leading to cracks. Fig 8 shows coefficient of linear expansion for several metals as a function of temperature.

**Thermal conductivity** Thermal conductivity of any material is defined as the heat transferred per unit time across a unit cross-sectional area along a unit thermal gradient. Thermal conductivity of materials, as seen in Fig 9, in general, decreases with decreasing temperature. It is an important property in cryogenics in view of the fact that heat transferred from surroundings to a cryogenic fluid depends on the thermal conductivity of materials of structural members, storage vessel, transport pipeline, insulation etc. A precise knowledge on thermal conductivity of different materials is necessary for the purpose of design of any cryogenic equipment

**Superconductivity** Superconductivity is another striking property of materials at cryogenic temperatures. After the great feat of helium liquefaction in 1908, Kamerlingh Onnes went on to discover the phenomenon of superconductivity in 1911. At a well-defined temperature  $T_c$ , called the transition temperature, in the absence of a magnetic field, many elements, alloys and compounds loses all electrical resistances and it is said to have become a superconductor. The resistance at  $T_c$  becomes so small that it can hardly be measured. Superconductivity occurs not only with metals and alloys, but also with some semiconductors and ceramic materials. Superconductivity is destroyed and the material behaves as a normal material if the magnetic field around it is increased beyond a threshold value called the critical field  $H_c$ . There are two types of superconductors: Type I and Type II. For Type I superconductors, there is a single value of the critical

field at which the transition from superconducting to normal behavior is abrupt. For Type II superconductors, there is a lower critical field  $H_{c1}$  at which the transition (to normal state) begins and an upper critical field  $H_{c2}$  at which the transition is complete. The magnetization curves are shown in Fig 10(a). Table 2 lists the transition temperature in zero field,  $T_c$  and the critical field at Absolute Zero,  $H_0$ . Critical field at any temperature  $T$  is given by  $H_c = H_0[1 - (T/T_c)^2]$ .

**Table 2: Transition properties of superconductors**

	Transition temperature in zero field, $T_c$ (K)	Critical field at Absolute Zero, $H_0$ (tesla)
Lead	7.19	0.0803
Niobium	9.2	0.1390 ( $H_{c1}$ ) 0.2680 ( $H_{c2}$ )
Mercury	4.15	0.415
Vanadium	5.41	0.0430 ( $H_{c1}$ ) 0.0820 ( $H_{c2}$ )
$Nb_3Al$	17.1	25.0 ( $H_{c2}$ )
$Nb_3Sn$	18.1	25
$Nb_3Al_{0.7}Ge_{0.3}$	20.7	44
$V_3Ga$	16.5	35
$Yba_2Cu_3O_7$	95.0	18.0 ( $H_{c2}$ )

In 1933, Meissner in Germany discovered that superconductors expel magnetic flux irrespective of whether field has been applied before the material has been cooled to the superconductive state or the field has been applied later. This is shown in Fig 10(b). This striking property allows a superconductor to float above a magnet without any visible support. This is the theory behind the fast-moving superconducting train.

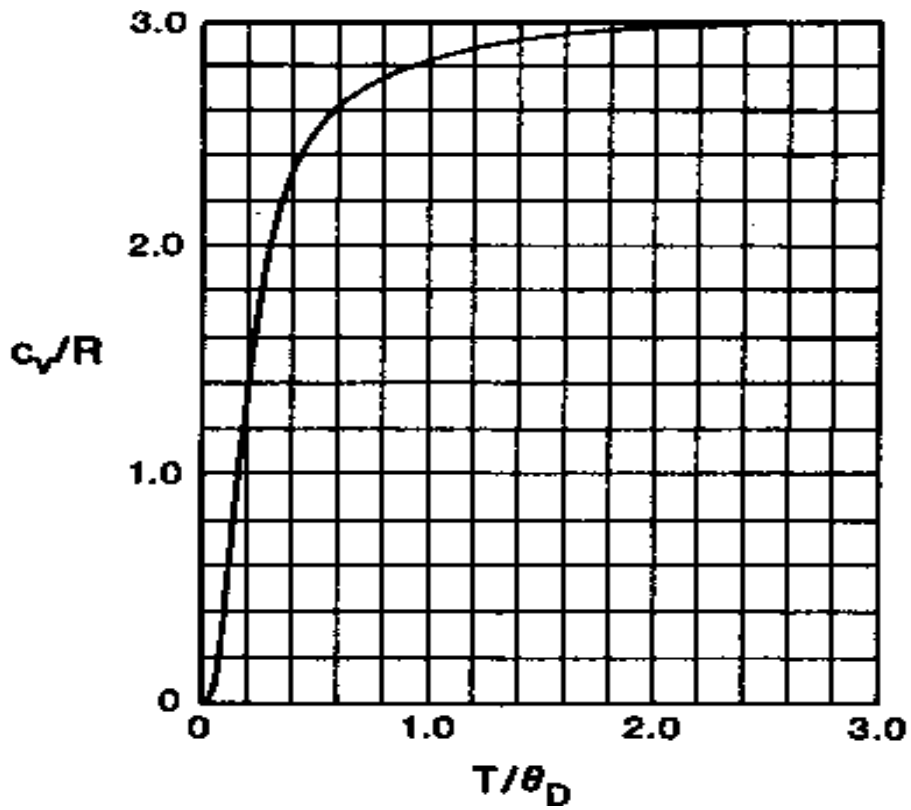


Fig 7: Variation of specific heat of mono-atomic crystalline solids at cryogenic temperatures

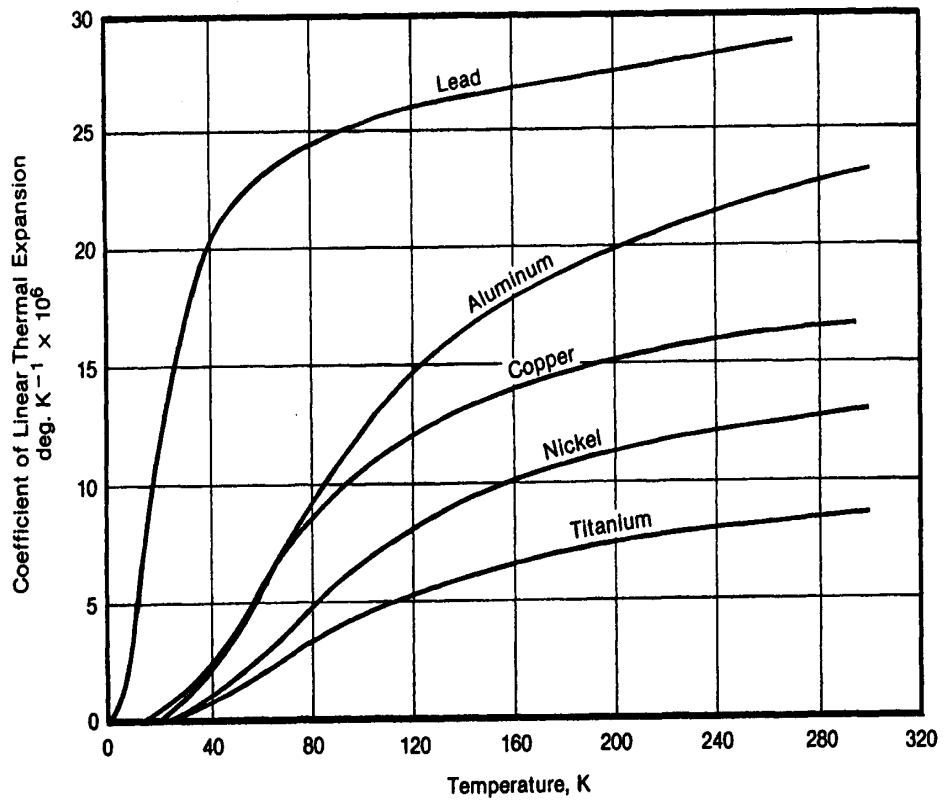


Fig 8: Coefficient of linear expansion for several metals as a function of temperature

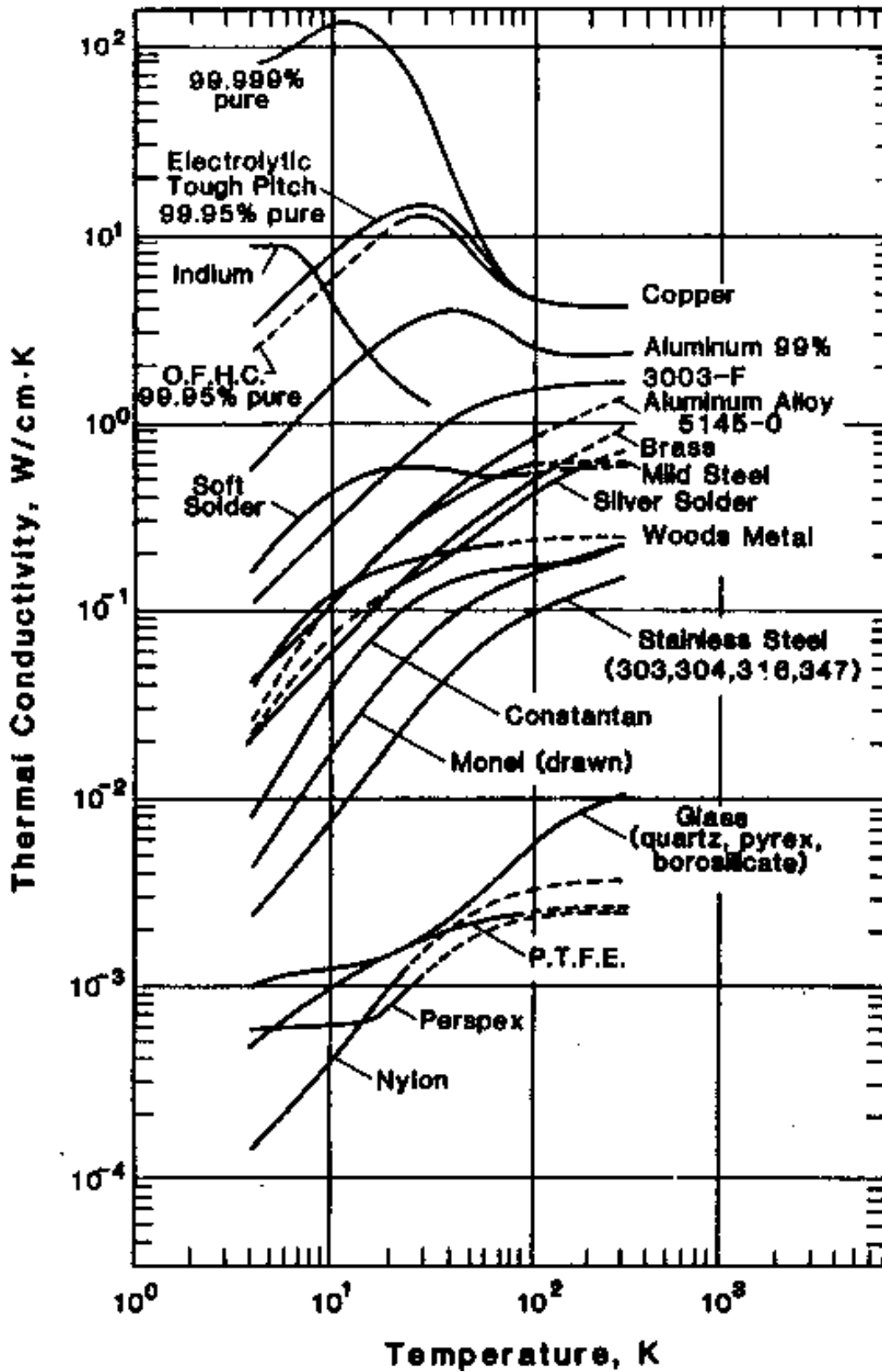
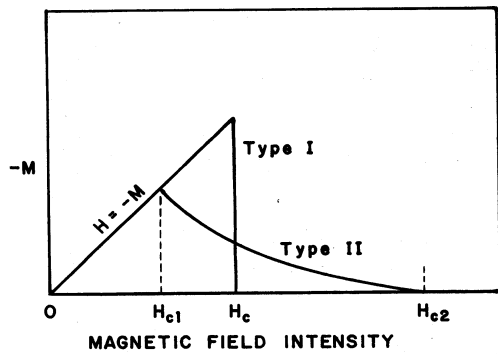
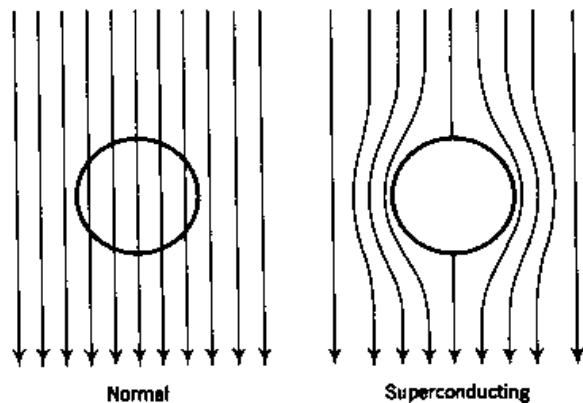


Fig 9: Thermal conductivity of some common solids



**Fig 10(a):** Variation of magnetization with applied



**Fig 10(b) :** The Meissner Effect

### INSULATION

The purpose of insulation is to reduce the flow of heat by introducing a higher resistance between the heat source and the heat sink. It requires energy to elevate the temperature above or reduce it below the ambient temperature. Therefore, a system, that has been heated or cooled, needs to be protected from the environment. One of the most important characteristics of high-temperature insulators is their thermal stability or their ability to withstand decomposition. While thermal conductivity remains the most important parameter for insulation, properties such as strength, rigidity, physical state and method of applications for an insulator are also important.

It is necessary to protect cryogenic fluids or cryogenic coldheads from the onslaught of environment surrounding them. In fact, it is the heat inleak into the system that prevented liquefaction of air or oxygen for a long time. It happened because the scientists could not see the liquid since it got evaporated as soon as it was produced. Cryogenics had to await the invention of double walled evacuated glass-vessel by Dewar (which was later marketed as now famous "thermos-flask" by some other people in Germany) in late nineteenth century to achieve holding of cryogenic liquids.

There are several reasons why insulation at cryogenic temperatures has to be dealt entirely separately. First, the power needed to produce cryogenic fluid or temperature is very high. Ideally, a refrigeration of 1000 W needs about 100 W of power input at  $0^\circ\text{C}$ , while the same refrigeration at liquid nitrogen and liquid helium temperature needs 3 kW and 75 kW of power input respectively. Further, radiation, that depends on the ratio of fourth power of absolute temperatures, becomes the dominant mode of heat transfer point in case of furnace heating as well as in case of cryogenics. The situation is more critical in case of cryogenics, because protecting liquid helium (4.2 K) from the environment (300 K) is more severe than protecting water (373 K) from Sun's environment (6000 K). Situation is further aggravated because of relatively lower latent heat of many cryogenic fluids.

Because of high temperature involved in furnace applications, inorganic insulation are used. For conventional refrigeration, both organic and inorganic insulations are employed. The list shown in Table 3 includes insulants for cryogenic applications, though some of them can be used for refrigeration and high temperature applications. The insulation strategy is to minimize radiative heat transfer, minimize convective heat transfer, and introduce a minimum of solid conductance media. Factors considered in the selection of the most suitable insulation include its ruggedness, convenience, volume, weight, ease of fabrication and handling, and, of course, thermal effectiveness and cost. In addition, one must consider the specific characteristics of the system under study and what constraint they put on the insulation choice. These system characteristics may include the type of liquid being stored or conveyed, the specific use of system, the environment surrounding the system, and the safety of the system. The most important properties of an insulating material are overall thermal conductivity of insulation, emissivity, moisture content, evacuability, porosity, and flammability.

In attempts to reduce the conduction component further, the space between double walled vessel or pipes storing or carrying cryogenic fluids is evacuated. In order to reduce the radiation component, aluminium-coated mylar sheets are put in layers under high vacuum and this insulation is called "Superinsulation". Therefore, creation and maintenance of vacuum remains another important area of cryogenics with respect to insulation in cryogenic systems. The various types of insulation used in the storage and transfer of cryogenic liquids can be classified into five categories: (1) Expanded foam insulation, (2) Evacuated Powder and Fibrous Insulation, (3) Vacuum Insulation, (4) Opacified Powder Insulation, (5) Multilayer Insulation.

**Table 3: Properties of insulants at atmospheric pressure (temperature limits 300 K and 77 K)**

Insulant	Bulk density kg/m <sup>3</sup>	Effective conductivity	thermal W/ mK	Comments	
Air	1.29		$2.6 \times 10^{-2}$	Only conduction taken into account	
Expanded Perlite	50		$2.6 \times 10^{-2}$		
Expanded Perlite	210		$4.4 \times 10^{-2}$		
Silica Aerogel	80		$1.9 \times 10^{-2}$		
Vermiculite	120		$5.2 \times 10^{-2}$		
Calcium Silicate (Synthetic)	360		$4.6 \times 10^{-2}$		
Asbestos	30		$4.7 \times 10^{-2}$		
Fibreglass Wool	110		$2.5 \times 10^{-2}$	Oil lubricants to be < 0.2% for oxygen use.	
Mineral Wool	130 to 320	$2.9$ to $4.3 \times 10^{-2}$			
Rock Wool	160		$3.5 \times 10^{-2}$		
Resin Bonded Fibreglass	30		$3.2 \times 10^{-2}$	Resin content < 4%	
Asbestos Board	140		$4.1 \times 10^{-2}$		
Balsa Wood	110		$4.9 \times 10^{-2}$		
Expanded Polystyrene	15		$2.4 \times 10^{-2}$		
Polyurethane Foam	49		$2.5 \times 10^{-2}$		
Foamed PVC Rigid	60		$2.5 \times 10^{-2}$		
Phenolic Syntectic Foam	310		$5.7 \times 10^{-2}$		
Urea Formaldehyde Foam	50		$3.0 \times 10^{-2}$		
Cork Board	110		$3.2 \times 10^{-2}$		
Perlite Fine	180		$0.95 \times 10^{-3}$	ALL PRESSURES IN INSULANTS BELOW $10^{-3}$ TORR	
Perlite Coarse	64		$1.9 \times 10^{-3}$		
Silica Aerogel	80		$1.6 \times 10^{-3}$		
Calcium Silicate Synthetic	210		$0.59 \times 10^{-3}$		
Silica Flour	200		$0.93 \times 10^{-3}$		
Basic Magnesium Carbonate	130		$0.71 \times 10^{-3}$		
Fibreglass random	50		$1.7 \times 10^{-3}$		
Fibreglass ordered fibres	240		$0.56 \times 10^{-3}$		
50:50 w/w Copper-Santocel	180		$0.33 \times 10^{-3}$		
40:60 w/w Al-Santocel	160		$0.35 \times 10^{-3}$		
Superinsulation	Layer density Layers/cm	Effective conductivity	thermal W/mK		
0.006 mm Aluminium Foil + 0.15 mm Fibreglass paper	20		$3.7 \times 10^{-5}$		ALL PRESSURES IN INSULANTS BELOW $10^{-5}$ TORR
Rayon net 2 mm mesh + Aluminium Foil 0.006 mm	10		$7.8 \times 10^{-5}$		
Nylon net 2 mm mesh + Aluminium Foil 0.006 mm	11		$3.4 \times 10^{-5}$		
NRC.2-Crinkled Aluminized Terelyne film 0.006 mm	33		$5.2 \times 10^{-5}$		
NRC.2-Crinkled Aluminized Terelyne film 0.006 mm	35		$4.2 \times 10^{-5}$		
Crinkled Aluminized Polyester	27		$2.9 \times 10^{-5}$		

Still air, with a density of  $1.29 \text{ kg/m}^3$  and a thermal conductivity of  $2.6 \times 10^{-2} \text{ W/mK}$ , appears to have a lower thermal conductivity than all other insulators. It may give an impression that air is preferable to glass wool as high temperature insulation. However, that is not the case in reality. Still air may have a lower conduction, but for glass wool and other insulants, where air is trapped in interstitial space and where the warm and cold surfaces do not face each other, the convection and radiation components are less and hence their "effective" thermal conductivity is less.

### APPLICATION OF CRYOGENICS AND ATMOSPHERIC GASES

There is hardly any field of engineering where cryogenics and atmospheric gases cannot be applied for the improvement of the product quality and for increasing the throughput and overall profitability. Within the limit of the length of this paper, it is neither possible to mention all of these uses nor it is possible to explain them in detail. However, some important ones would find mention here.

#### Mechanical Engineering

**Cryogenic size reduction** Cryogenic grinding enables materials to be ground into fine particles at low temperatures. By using cryogenic temperatures, materials become brittle, enabling easy fracture into small particle size. The use of liquid nitrogen not only enables size reduction but also aids in increased processing throughput. Benefits of cryogenic size reduction are as follows: improved size reduction, production of fine powders, reduced heat build up, higher production and reduced operating costs, practical recycling and inert atmosphere. The following are the application areas of cryogenic size reduction:

- In polymer processing, one must reduce the size of heat-sensitive raw materials or products during production or recycling.
- In powder coating one must produce polymer powders that have consistent particle size and shape to produce uniform quality coatings on automotive, plumbing, and structural products.
- In the production of color concentrate where it is needed to produce powders of concentrated color for use as polymer additives/colorants. These colorants must have consistent color and controlled particle size.
- In recycling of rubber where one requires fine particle sizes in order to allow the material to be reformulated or reincorporated into primary products, generally via a molding process.
- Production of hot melt adhesives need to process materials with low softening and melting temperatures onto fine particles to permit extrusion of custom shapes and sizes for glue guns.
- Cryogenic Size Reduction (grinding) of spices is an acceptable technique that helps to retain the natural

quality of spices. Use of liquid nitrogen provides the required low temperature so that volatile oils which preserve the spice flavour retains during grinding process.

Many commercially produced thermoplastic polymers are difficult to grind at ambient temperature. These plastic are tough and throughout the process the material heats up. The higher temperature causes the materials to agglomerate, which results in tackiness and adhere to the cutting blades or mills. On reduction the temperature of the plastic materials, their properties change from tough, tacky and ductile to hard and brittle. A brittle plastic or polymer can be easily and quickly shattered into reduced particle sizes when subjected to the impacts of hammermills. Examples of plastic material which are generally subjected to cryogenic grinding are thermosets, elastomers, plastic colour concentrates, etc.

**Cryoshrinking** Shrink fitting iron rings over wooden wheel for carts by expanding it on heating was a well known technique to our ancestors. Though shrink fitting was traditionally performed by heating the outer components (wheels, rotors or housing) to allow easy fitting of the inner part (shaft, bushes or bearings), in recent years ready availability of cryogenic refrigerant (like liquid nitrogen) has increased the prospect of converse method, where the inner part is strongly cooled and contracted sufficiently for easy fitting into the unheated outer part. This contraction of inner region using cryogen for fitting purpose is known as cryoshrinking. The cryoshrinking process is mostly applied in different mechanical applications such as in railway locomotives and other engines where shafts, bushes, wheels or rotors etc. are involved.

The special advantages of cooling inner part rather than heating outer part for shrink fittings are generally the following: Cryogenic method is quick. Power consumption is lesser for smaller volume and hence mass of inner part. It needs minimum special equipment. It results minimum metallurgical or other changes in the component being assembled.

**Oxy-acetylene Welding** Oxy-Acetylene welding relies on the heat of a flame to melt the material being welded. Fusion can either be autogenous or with the addition of a filler material. The high flame temperature required for oxy-fuel welding and cutting processes is obtained by combining oxygen with a fuel gas to produce flame temperatures of approximately  $2500^\circ\text{C}$  to  $3000^\circ\text{C}$ . The heat source for this process is a chemical reaction resulting from the combustion of acetylene with oxygen. This is an exothermic reaction in which equal volumes of acetylene and oxygen supplied by the blowpipe react to produce carbon monoxide, and hydrogen as products of the first stage of combustion.

**Oxyfuel gas-cutting** Oxyfuel gas cutting (OFC) is a group of oxygen cutting processes that use heat from an oxyfuel gas flame. The necessary temperature is

maintained by means of gas flames obtained from the combustion of a fuel gas and oxygen. There are a number of fuel gases used. The most popular is acetylene. Natural gas is widely used, as is propane. Hydrogen is rarely used. Gasoline can even be used but is not popular. Each fuel gas has particular characteristics and may require slightly different apparatus because of this characteristic. The general concept of oxyfuel gas cutting is similar no matter what fuel gas is used. It is the oxygen jet that makes the cut in steel, and cutting speed depends on how efficiently the oxygen reacts with steel. Oxygen for cutting must be 99 % pure. If purity is less, cutting speed and efficiency will be reduced.

### Civil Engineering

**Ground Freezing** Problems are often encountered during the construction of large cofferdams, mineshafts and tunnels in soft soil or in a busy metropolis, when large quantity of water seeps in, soft soil collapses and foundations of nearby structures developed cracks. This problem can be avoided by applying techniques of ground freezing, when the pore water in soil is frozen to ice, thus becoming strong enough to support the structures purely on a temporary basis.

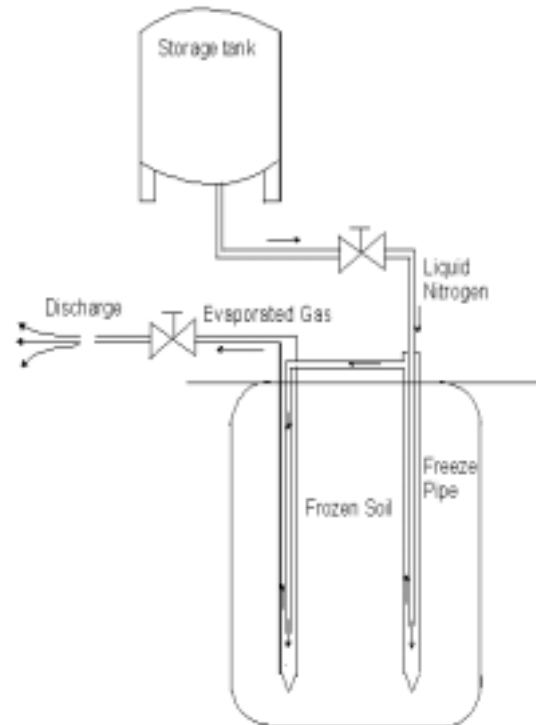
Application of these techniques has wide ranging advantages in preventing ecological hazards with draw down of the ground water table, collapsing of historical monuments and reduction of project execution time in constructing soft soil tunnels and cofferdams.

Ground freezing is done by installing coaxial pipes into the ground down to the desired depth as predetermined distance to each other, generally in a circular fashion. The inside coaxial pipe called feed pipe, supplies coolant such as brine or liquid nitrogen. The coolant flows down the inside freeze pipe and comes up through the annulus formed by two pipes. The warmed up liquid flows back to the refrigeration plant in case of brine, where as in case of liquid nitrogen the sensible heat of nitrogen is also extracted in subsequent two or three pipes and then the gas is exhausted in atmosphere. The frozen soil forms a continuous, impervious wall that does not allow any water to seep in and is of sufficient strength to withstand the load of adjoining soil and structures.

After the necessary excavation or construction is done, the soil is allowed to thaw and it reverts to its original structure. The general procedure for design is to determine if the ground is suitable for the freezing method by conducting a site investigation, then to select a structurally stable configuration for the retaining structure and finally to design the freeze pipe arrangement together with the refrigerant requirement.

### Food Technology

**Food Freezing** Food freezing by mechanical refrigeration is slow, which results in deterioration of cell structure of the foodstuff. The rupture of cell structure causes the deterioration of quality, texture, color, taste and flavor of food. Mechanical devices are expensive to buy, are bulky, and require around-the-clock maintenance and supervision. The difficulties of



**Fig 11: Simplified schematic diagram of ground freezing**

food freezing using freon refrigeration technique can be overcome adopting liquid nitrogen freezing process or cryo-freezing process. Since the liquid nitrogen temperature is extremely low, the liquid nitrogen freezing is 10 times faster than air blast freezing and the water content in food stuff does not get sufficient time to form big ice crystal. Therefore stress developed on cell membrane of food is negligibly small with respect to refrigeration food freezing process involving formation of large ice crystal. As the cell structure in liquid nitrogen freezing process does not change appreciably, the quality, texture, taste, etc. remains as it was in fresh food.

### Medical Applications

**Cryosurgery** Cryosurgery is a technique that destroys cancer by freezing the cells. It has been used at some top medical centers for tumors of the prostate, liver, lung, breast and brain as well as for cataracts, gynecological problems and other diseases. Freezing temperatures of a cryogenic agent applied directly or indirectly to the skin cause local destruction of tissue. Certain conditions may require multiple or repeated



treatments. Cryotherapy, a term used for many years, is best reserved for more superficial forms of freezing. While the mechanisms of how cryosurgery destroys cells are still being investigated, available evidence suggests that several processes contribute together. First, the creation of intracellular ice is lethal to nearly all cells. Rapid temperature loss enhances the formation of intracellular ice. Secondly, as ice forms around a cell, the free water inside the cell is drawn off, shrinking the cell and collapsing many of the walls or membranes inside the cell, releasing proteins or chemicals that can be toxic. Finally, as ice, which surrounds shrunken cells, begins to thaw, large amounts of free water produced by the thawing ice will rush back inside the cells, causing them to burst. Thus, it is believed by some that the physical features of cryosurgery which are most important in producing extensive cell destruction include rapid freezing to very low ( $-195^{\circ}\text{C}$ ) temperatures, and a slow thawing.

**Cryosurgery of the prostate** Cryosurgery of the prostate represents an effort by a surgeon to destroy tumor cells in the prostate by freezing them, rather than surgically removing them (i.e. via radical prostatectomy) or radiating them (i.e. via external beam radiotherapy, or placing radioactive seed implants into the prostate).

**Cryosurgery of Liver** Doctors at the UT Southwestern Medical Center at Dallas say cryosurgery is a treatment option for liver cancer patients who can't be treated by more traditional surgical approaches. These patients include those who have multiple liver tumors, those whose tumors are near major blood vessels and those whose condition makes liver resection especially risky. Surgeons use ultrasound to guide a probe through the liver to the tumor. They use liquid nitrogen to chill the probe tip to nearly  $-196^{\circ}\text{C}$ . The probe kills the tumor by freezing it. The dead tumor is then eventually absorbed into the surrounding tissue. This is a very localized treatment, so there is little damage to surrounding tissues. There also is less blood loss with this procedure than with traditional liver surgery.

**Cryosurgical probes** Development of closed cryosurgical probe has enabled doctors to control both the gas flow and the temperature of the gas. The probe is usually cooled by Joule-Thomson principle of a rapid expanding gas like nitrous oxide or by allowing liquid nitrogen to become gaseous at cryotrip. In the probe based on Joule-Thomson principle (Linde Cycle), the gas under pressure is fed through the inner of two concentric tubes (SS) and passes through a micro-orifice where it expands and impinges on the inner wall of the probe tip.

**Cryosurgery of skin cancer** Cryosurgery gets rid of abnormal or diseased tissue by freezing it, usually with liquid nitrogen. Growths on the skin such as warts, moles, and some kinds of skin cancer are often removed

with cryosurgery. In most cases, liquid nitrogen is put on the growth with a large cotton-tipped swab until freezing destroys it. Sometimes liquid nitrogen is sprayed on the area.

Shortly after the procedure, the treated area becomes red and swollen, and within 2 or 3 days, a blister forms over it. The blister, which may contain a small amount of blood, will break by itself in about 2 weeks, and may leave a scab. After the area is totally healed, there should have little or no scarring.

## Chemical Engineering

**Pulp and Paper Production** Paper industry has long used chemical methods of bleaching pulp for paper. The oxidants used help to create a clean, white paper pulp for processing into paper. The problem with using chemical oxidants to remove the color of the processing pulp is that the chemicals then must be discarded. New interest in keeping chemical discharge to a minimum has caused pulp processors to look at alternative ways to bleach their product. One of these ways is through the use of oxygen or rather ozone (allotrope of oxygen).

**Waste Water Treatment** We use water for showers, baths, toilets, washing dishes and clothes, and many other activities. If our sewage isn't properly treated, we could be contributing to the posting of the "No Swimming--No Fishing" sign. If it is not properly cleaned, water can carry disease. Since we live, work and play so close to water, the vast majority of the potentially harmful bacteria have to be removed to make sure the water returning to waterways is clean. Clean water is safe water. Thus waste water is to be treated for its reuse. Oxygen or ozone plays a major role in treating waste water.

**Glass and Optical Fiber Manufacturing** With abundance of oxygen supply, oxy-fuel combustion used as a replacement for air-based glass melting, reduces nitrogen oxide emissions to meet tightening regulations, while contributing to improved glass quality and increased productivity. The use of oxygen in furnace firings offers other benefits, including shorter furnace rebuild times and easier furnace maintenance. Gaseous helium is critical for producing optical fibres used in telecommunication cables, a key component of the information highway, which carries vast amounts of data.

**Cryogenic processing of Used Tire** The automobile or track tire has been one of the more difficult items to recycle - or even worse - to discard. This resulted in billions being discarded along the countryside, behind buildings, in the woods, or anywhere. Cryogenic provides the necessary technology for the effective recovery, separation, and reuse of all materials used in the tire. In fact, the use of cryogenics is the only known way to recover the rubber from the steel radial tire.

## Electrical Engineering

### Superconducting Magnetic Energy Storage (SMES)

Many transmission lines are limited in power capacity by stability considerations, even more so as transmission networks become heavily interconnected. Because of its fast response to inject or absorb power, an SMES plant can significantly enhance the stability of a transmission line. SMES is a relatively simple concept. It stores electric energy in the magnetic field generated by DC current flowing through a coiled superconducting wire. SMES system requires a large quantity of liquid helium in order to maintain the whole system in superconducting state.

### Cryogenics in Semiconductor and Integrated Chip Development

A semiconductor is a class of crystalline solids that conduct electricity. The electrical properties of materials such as single-crystal silicon, germanium, and gallium arsenide are extremely sensitive to the presence of impurities. By controlling the concentration and type of impurities (dopants), such as phosphorus and boron in silicon, electrical conductivity can be controlled. A reliable supply of high purity gases is critical to advanced semiconductor manufacturing. The silicon on which most ICs are made is itself an ultrahigh purity product. The wafer fabrication requires a manufacturing environment with gas of ultrahigh purity that is cleaner by far than, for example, a hospital operating theatre. Ultra-clean gas technology has grown up largely to meet semiconductor needs. These include nitrogen, produced on-site by separation of air; oxygen, produced on-site or delivered as cryogenic liquid; argon, delivered as cryogenic liquid; and hydrogen, either produced on-site or delivered as a cryogenic liquid or compressed gas.

## Cryogenic Propulsion

**Cryogenic Rocketry** In order for a satellite to go into orbit it must accomplish two major tasks. First, the satellite must rise above the atmosphere that surrounds the Earth's surface. A propulsion device must strain against gravity to rise above the atmosphere. Second, the satellite must also be provided with enough horizontal velocity above the atmosphere to at least equal the local circular speed upon orbital injection otherwise it will reenter the atmosphere and burn due to friction. Both these jobs are done by rockets. As the development of rocket engines continued, higher thrust levels were achieved when liquid oxygen and liquid hydrogen were used as fuel. This allowed for the construction of the first intercontinental rocket with a range of more than 10,000 km.

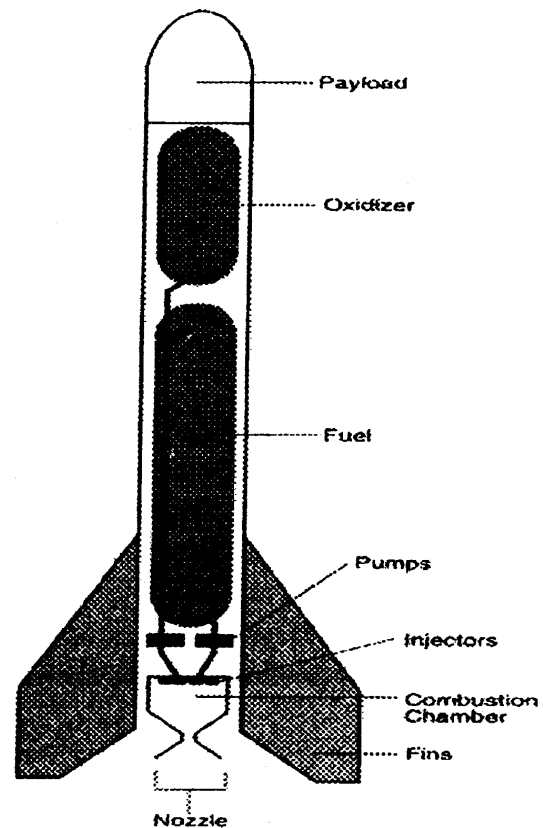
**Components of cryogenic Rocket** The major components of a liquid fuel cryogenic engine are the thrust chamber, the fuel pumps with its valves and regulators and the tanks. The fuel and oxidizer pump system is the main component and can be divided into

two different principles. The simple way is to increase the pressure of the tank with inert gases to pressurize the tanks against the pressure in the combustion chamber. In this type of engine the fuel and gas tanks are very heavy, which explains why this design principle is only used for smaller rockets with shorter burning times. For the above-mentioned liquid hydrogen and oxygen cryogenic fuel, it is not an option at all because of the hydrogen's low density and the corresponding large fuel tank size.

### Working Principle of Liquid Propellant Rockets

The other main kind of rocket engine is one that uses liquid propellants. This is a much more complicated engine, as is evidenced by the fact that solid rocket engines were used for at least seven hundred years before the first successful liquid engine was tested. Liquid propellants have separate storage tanks - one for the fuel and one for the oxidizer. They also have pumps, a combustion chamber, and a nozzle.

The fuel of a liquid-propellant rocket is usually kerosene or liquid hydrogen; the oxidizer is usually liquid oxygen. They are combined inside a cavity called the combustion chamber. High-pressure turbo-pumps provide an example of the rocket engine. Here the propellants burn and build up high temperatures



Liquid Propellant Rocket

Fig 12: Layout of Liquid Propellant rocket

and pressures, and the expanding gas escapes through the nozzle at the lower end. To get the most power from the propellants, they must be mixed as completely as possible. Small injectors (nozzles) on the roof of the chamber spray and mix the propellants at the same time. Because the chamber operates under high pressures, the propellants need to be forced inside. Powerful, lightweight turbine pumps between the propellant tanks and combustion chambers take care of this job. With any rocket, and especially with liquid-propellant rockets, weight is an important factor. In general, the heavier the rocket, the more the thrust needed to get it off the ground. Because of the pumps and fuel lines, liquid engines are much heavier than solid engines.

One especially good method of reducing the weight of liquid engines is to make the exit cone of the nozzle out of very lightweight metals. However, the extremely hot, fast-moving gases that pass through the cone would quickly melt thin metal. Therefore, a cooling system is needed. A highly effective though complex cooling system that is used with some liquid engines takes advantage of the low temperature of liquid hydrogen. Hydrogen becomes liquid when it is cooled to  $-253^{\circ}\text{C}$  (20 K). Before injecting the hydrogen into the combustion chamber, it is first circulated through small tubes that lace the walls of the exit cone. In a cutaway view, the exit cone wall looks like the edge of corrugated cardboard. The hydrogen in the tubes absorbs the excess heat entering the cone walls and prevents it from melting the walls away. It also makes the hydrogen warmer because of the heat it picks up. We call this kind of cooling system regenerative cooling.

### Metallurgical Engineering

**Steel making** Steel is an alloy of iron, carbon, and small proportions of other elements. Steel-making involves the removal of iron's impurities and the addition of desirable alloying elements. Earlier processes of steel-making involved a huge amount of fuel (air) and thus a huge power consumption which in turn enhanced the cost of steel. After the availability of cryogenically prepared oxygen in industrial scale, LD process became common in 1950s where large amount of oxygen was being used. This process has reduced the cost of steel abruptly and lifted up our civilization a couple of steps forward.

**Copper extraction** Copper is an abundant metallic element which is found in many locations. Copper occurs in native form (i.e. as nuggets of the free metal) and in oxide ores (e.g. cuprite,  $\text{Cu}_2\text{O}$ ) and in sulphide ores (e.g. chalcocite,  $\text{CuS}_2$ , and Chalcopyrite,  $\text{CuFeS}_2$  or  $\text{Cu}_2\text{S}\cdot\text{Fe}_2\text{S}_3$  and Bornite,  $\text{Cu}_3\text{FeS}_3$ ).

Oxygen or oxygen enriched air is being widely used to extract copper from its ores.. Different processes of

copper extraction have been successfully developed where oxygen plays a major role.

**Zinc extraction** Oxygen has its wide application in extraction of zinc from its ores. Some important naturally available ores of zinc are sphalerite ( $\text{ZnS}$ ), zincite ( $\text{ZnO}$ ) etc. with the association of several compounds like of sulphides of Cu, Cd etc. Different floatation techniques are employed to separate sulphide of Pb, Cu and Zn from typical zinc ores. Extraction of zinc from its sulphide ores are basically carried out both by pyro-metallurgical and hydro-metallurgical techniques. The former is mainly adopted if the concentrate is of very high grade.

### SAFETY IN HANDLING CRYOGENS

#### Types of Hazards

The low temperature and relatively high density of cryogenics can cause safety concerns. Hazards in the handling of these fluids can arise in several ways. The low temperature can freeze living tissue, a phenomenon that has been referred to as cryogenic "burns" or frostbite. Cryogenic temperatures can also affect structural materials by causing embrittlement and can also induce unwanted stresses either as a result of the unavoidable thermal contraction or even as a result of thermal gradients within a structure. The cryogenics have the ability to condense and solidify substances, such as water vapor or carbon dioxide, that freeze at a higher temperature, and this can cause safety problems if the resulting solids can block safety relief passages, or if they can cause erosion in places like valve seats. The great expansion that can take place when a cryogen evaporates can cause substantial displacement or dilution of the oxygen content of the local atmosphere. If the expansion is not allowed, enormous pressures can build up. In the case of some cryogenics, their capability to participate in chemical reactions, such as combustion, or their toxic nature can result in additional hazards.

**Cold damage to living tissue** The low temperature of cryogenics can cause serious damage to living organisms. The injury can be immediate in the case of direct contact with a cold fluid or with equipment that has been cooled to cryogenic temperature. In addition, the more gradual cooling that may be caused by being subjected to a very cold atmosphere for an extended period of time can also cause physical harm by inducing hypothermia.

**Freezing of tissue** Direct contact with cryogenic fluids (liquid or cold gas) or cold equipment can cause serious damage to living tissue. Although cellular changes start to occur at tissue temperatures as high as  $15^{\circ}\text{C}$ , the formation of ice crystals in the tissue does not occur until the tissue is cooled to about  $-3^{\circ}\text{C}$  because of the freezing-point lowering caused by dissolved solutes. When the tissue temperature is low enough, ice crystals begin to form outside of the cell walls. Water is then

transferred from the inside of the cell, through the cell wall, resulting in cell dehydration and cell damage similar to that caused by thermal burns. For this reason, the tissue damage caused by freezing is sometimes referred to as a "cryogenic burn" as well as "frostbite." Further cell damage can occur as cells are deformed by ice crystals and osmotic pressure. As the tissue temperature is lowered, the decreased blood flow can result in tissue necrosis and, possibly, gangrene. However, records of such damage show that tissue injury as a result of cryogen spills is rare.

Although it has been demonstrated that a very brief contact with liquid nitrogen, for example, does not necessarily cause any harm to the skin, such a practice is not recommended by anyone without a great deal of experience in the handling of cryogenic fluids. It is true that for very brief periods (one or two seconds) of gentle contact (no rapid flow) with small quantities, the liquid nitrogen does not directly contact the tissue because of the large temperature difference between the skin and the fluid. This temperature difference causes the formation of a gas film, and heat transfer to the skin occurs in the film-boiling regime, where the heat transfer is somewhat slower. However, in spite of this apparent protection, prolonging the contact any longer than a second or two can be sufficient to produce serious tissue freezing. If the fluid (either liquid or cold gas) is traveling with a significant velocity, freezing can occur almost immediately. Another way in which freezing can be almost instantaneous is by contact with uninsulated, cold metal or other cold equipment. In this case, there is no formation of a gas film between the cold metal surface and the skin, and the heat transfer is much more rapid.

**Hypothermia** In a case where prolonged exposure to a very large spill could occur, lowering of the body temperature is a serious possibility. Body temperature is a function of the production of heat within the body and the heat loss from the body. Body heat is produced by metabolism, muscle activity, and shivering. When the body is incapable of producing heat at a rate equal to the rate of heat removal, hypothermia results. At a body core temperature below 35°C, generalized organ dysfunction and central nervous system, cardiac, and respiratory depression occur. At a lowering of the body core temperature below 28°C, ventricular fibrillation becomes more likely. Thus, even a minor decrease in body core temperature is serious, and the consequences become more drastic as the lowering of the temperature progresses.

**Asphyxiation** A large expansion takes place upon the evaporation of a cryogenic fluid. An additional expansion occurs upon the gas warming to ambient temperature. There is some variation from one cryogen to the next in the actual volume ratios to be expected; however, for rule-of-thumb estimates, a factor of 1000 is frequently used as the ratio of the volume of the gas

formed at ambient temperature and standard atmospheric pressure to the volume of the same mass of cryogen as a liquid. Consequently, the spill of a large quantity of a cryogen in a confined space can lead to an atmosphere that does not support life.

When working with a cryogenic liquid in a closed room, it is necessary to determine the maximum quantity of liquid that could be released under any circumstance and to estimate the maximum depletion of the oxygen in the room that could occur as a consequence of that release. For example, the instantaneous spill of a common-size Dewar of liquid nitrogen (160 liters) in a laboratory with dimensions of 5 m by 7 m by 3 m high would produce sufficient ambient-temperature gas to completely replace the entire room atmosphere, thus rendering the local atmosphere totally inert and incapable of supporting life. If the spill were to take place slowly, it is possible that the evolved gas would thoroughly mix with the room atmosphere, with the result that the equilibrium mixture would be, expelled from the room. This complete mixing would result in a lesser decrease in the room's oxygen content. However, without additional ventilation, even in this case the oxygen content would decrease to less than 8%, still creating a lethal atmosphere. If the cryogen's release or spill rate can be predicted and complete mixing could be assumed, a ventilation rate that would prevent the oxygen content of the room's atmosphere from becoming dangerously low could be calculated. However, if the ventilation rate is not sufficient to thoroughly mix the atmosphere at all points in the room, pockets of lethal atmosphere can still exist.

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