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Cryogenics

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CRYOGENICS

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CRYOGENICS

INTRODUCTION:

We will start by defining the term Cryogenics:

Cryogenics is the science that addresses the production and effects of very low temperatures. The word originates from the Greek words 'kryos' meaning "frost" and 'genic' meaning "to produce." Under such a definition it could be used to include all temperatures below the freezing point of water (0° C). Professor Kamerlingh Onnes of the University of Leiden in the Netherlands first used the word in 1894 to describe the art and science of producing much lower temperatures. He used the word in reference to the liquefaction of permanent gases such as oxygen, nitrogen, hydrogen, and helium. Oxygen had been liquefied at -183° C a few years earlier (in 1887), and a race was in progress to liquefy the remaining permanent gases at even lower temperatures. The techniques employed in producing such low temperatures were quite different from those used somewhat earlier in the production of artificial ice. Very efficient heat exchangers are required to reach extremely low temperatures required for liquefaction. Over the years the term cryogenics has generally been used to refer to temperatures below approximately -150°C.

It is a very important technology and part of our daily lives even if we seldom know of its application. We definitely use the application and benefits of this basic science in ways now seemingly commonplace. Let us now take a very brief look at several benefits from this marvelous technology.

BENEFITS OF CRYOGENIC PROCESSES:

Varying applications of cryogenic technology have provided significant benefits and made possible the following advances in technology:

- Super-cooling devices used for: 1.) The Large Hadron Collider at CERN, 2.) Ship propulsion motors, 3.) Experimental fusion reactors and 4.) Whole-body MRI scans.
- One of the most used purpose for “super-cooling” is stress relief and treatment of steels. The benefits of this technology are given as follows:
 - Reduces abrasive and adhesive wear. Treated material typically yields two to three times the production of non-treated material
 - Permanently changes the structure of the metal resulting in improved machining properties. Treated components may be ground after treatment, and the benefits of treatment are retained.

- Reduce the frequency and cost of tool remanufacture. Worn treated tools require less material removal to restore a uniform cutting edge. Furthermore treated tools may be reground more times before falling below the minimum acceptable dimensions.
 - Substantially reduce machine downtime caused by tool replacement.
 - Improved surface finishing on material being manufactured with treated tooling. Treated tooling stays sharper and in tolerance longer than untreated.
 - Reduces likelihood of catastrophic tool failures due to stress fracture.
 - Stress relieve to reduce inherit/residual stress caused by manufacture.
 - Increases the overall durability of the treated product.
- Fast freezing of foods
 - Preservation of biological materials such as livestock semen as well as human blood, tissue, and embryos.
 - The practice of freezing an entire human body after death in the hope of later restoring life is known as cryonics. **This process is not an accepted scientific application of cryogenics.**
 - The freezing of portions of the body to destroy unwanted or malfunctioning tissue is known as cryosurgery. It is used to treat cancers and abnormalities of the skin, cervix, uterus, prostate gland, and liver.
 - Superconductivity of metals
 - Stem Cell Research
 - Liquefaction of Gases (NOTE: Liquefaction of gases is a tremendous industry and one which brings billions of currency to world markets.)

I would like to go a little deeper into the most viable “commercial” uses of cryogenic technology. These uses are as follows:

COMMERCIAL USES OF CRYOGENICS

FOOD PROCESSING

Freezing is one of the oldest and most widely used methods of food preservation. This process allows preservation of taste, texture, and nutritional value in foods better than any other method. The freezing process is a combination of the beneficial effects of low temperatures at which microorganisms cannot grow, chemical reactions are reduced, and cellular metabolic reactions are delayed. Cryogenics is the most often used method to accomplish this food preservation.

The importance of freezing as a preservation method

Freezing preservation retains the quality of agricultural products over long storage periods. As a method of long-term preservation for fruits and vegetables, freezing is generally regarded as superior to canning and dehydration, with respect to retention in sensory attributes and nutritive properties (Fennema, 1977). The safety and nutritional quality of frozen products are emphasized when high quality raw materials are used, good manufacturing practices are employed in the preservation process, and the products are kept in accordance with specified temperatures.

The need for freezing and frozen storage

Freezing has been successfully employed for the long-term preservation of many foods, providing a significantly extended shelf life. The process involves lowering the product temperature generally to -18 °C or below. The physical state of food material is changed when energy is removed by cooling below freezing temperature. The extreme cold simply retards the growth of microorganisms and slows down the chemical changes that affect quality or cause food to spoil.

Competing with new technologies of minimal processing of foods, industrial freezing is the most satisfactory method for preserving quality during long storage periods. When compared in terms of energy use, cost, and product quality, freezing requires the shortest processing time. Any other conventional method of preservation focused on fruits and vegetables, including dehydration and canning, requires less energy when compared with energy consumption in the freezing process and storage. However, when the overall cost is estimated, freezing costs can be kept as low (or lower) as any other method of food preservation.

Current status of frozen food industry in U.S. and other countries

The frozen food market is one of the largest and most dynamic sectors of the food industry. In spite of considerable competition between the frozen food industry and other sectors, extensive quantities of frozen foods are being consumed all over the world. The industry has recently grown to a value of over US\$ 75 billion in the U.S. and Europe combined. This number has reached US\$ 27.3 billion in 2001 for total retail sales of frozen foods in the U.S. alone. In Europe, based on U.S. currency, frozen food consumption also reached 11.1 million tons in 13 countries in the year 2000.

Advantages of freezing technology in developing countries

Developed countries, mostly the U.S., dominate the international trade of fruits and vegetables. The U.S. is ranked number one as both importer and exporter, accounting for the highest percentage of fresh produce in world trade. However, many developing countries still lead in the export of fresh exotic fruits and vegetables to developed countries.

For developing countries, the application of freezing preservation is favorable with several main considerations. From a technical point of view, the freezing process is one of the most convenient and easiest of food preservation methods compared with other commercial preservation techniques. The availability of different types of equipment for several different food products results in a flexible

process in which degradation of initial food quality is minimal with proper application procedures. As mentioned earlier, the high capital investment of the freezing industry usually plays an important role in terms of economic feasibility of the process in developing countries. As for cost distribution, the freezing process and storage in terms of energy consumption constitute approximately 10 percent of the total cost. Depending on the government regulations, especially in developing countries, energy cost for producers can be subsidized by means of lowering the unit price or reducing the tax percentage in order to enhance production. Therefore, in determining the economical convenience of the process, the cost related to energy consumption (according to energy tariffs) should be considered.

Food items	Sales US\$ (million)	% Change vs. 2000
Total Frozen Food Sales	26600	6.1
Baked Goods	1400	9.0
Breakfast Foods	1050	4.1
Novelties	1900	10.5
Ice Cream	4500	5.7
Frozen Dessert/Fruit/Toppings	786	5.4
Juices/Drinks	827	-9.7
Vegetables	2900	4.3

TABLE 1: Frozen food industry in terms of annual sales in 2001

(Source: Information Resources)

Today in modern society, frozen fruits and vegetables constitute a large and important food group among other frozen food products. The historical development of commercial freezing systems designed for special food commodities helped shape the frozen food market. Technological innovations as early as 1869 led to the commercial development and marketing of some frozen foods. Early products saw limited distribution through retail establishments due to insufficient supply of mechanical refrigeration. Retail distribution of frozen foods gained importance with the development of commercially frozen vegetables in 1929.

The frozen vegetable industry grew primarily after the development of scientific methods for blanching and processing in the 1940s. Only after the achievement of success in stopping enzymatic degradation, did frozen vegetables gain a strong retail and institutional appeal. Today, market studies indicate that

considering overall consumption of frozen foods, frozen vegetables constitute a very significant proportion of world frozen-food categories (excluding ice cream) in Austria, Denmark, Finland, France, Germany, Italy, Netherlands, Norway, Sweden, Switzerland, UK, and the USA.

Commercialization history of frozen fruits is older than frozen vegetables. The commercial freezing of small fruits and berries began in the eastern part of the U.S. in about 1905. The main advantage of freezing preservation of fruits is the extended usage of frozen fruits during off-season. Additionally, frozen fruits can be transported to remote markets that could not be accessed with fresh fruit. Also, freezing preservation makes year-round further processing of fruit products possible, such as jams, juice, and syrups from frozen whole fruit, slices, or pulps. In summary, the preservation of fruits by freezing has clearly become one of the most important preservation methods.

SUPERCONDUCTIVITY

Superconductivity: Properties, History, Applications and Challenges

Superconductors differ fundamentally in quantum physics behavior from conventional materials in the manner by which electrons, or electric currents, move through the material. It is these differences that give rise to the unique properties and performance benefits that differentiate superconductors from all other known conductors. Superconductivity is accomplished by using cryogenic methodology.

Unique Properties

- Zero resistance to direct current
- Extremely high-current-carrying density
- Extremely low resistance at high frequencies
- Extremely low signal dispersion
- High sensitivity to magnetic field
- Exclusion of externally applied magnetic field
- Rapid single flux quantum transfer
- Close to speed of light signal transmission

Zero resistance and high-current density have a major impact on electric power transmission and also enable much smaller or more powerful magnets for motors, generators, energy storage, medical equipment and industrial separations. Low resistance at high frequencies and extremely low signal dispersion are key aspects in microwave components, communications technology and several military applications. Low resistance at higher frequencies also reduces substantially the challenges inherent to miniaturization brought about by resistive, or I²R, heating. The high sensitivity of superconductors to magnetic field provides a unique sensing capability, in many cases 1000x superior to today's best conventional measurement technology. Magnetic field exclusion is important in multi-layer electronic

component miniaturization, provides a mechanism for magnetic levitation and enables magnetic field containment of charged particles. The final two properties form the basis for digital electronics and high speed computing well beyond the theoretical limits projected for semiconductors. All of these materials properties have been extensively demonstrated throughout the world.

STEM CELL RESEARCH AND USAGE

Cryopreservation of Haematopoietic Stem Cells

This routine procedure generally involves slow cooling in the presence of a cryoprotectant to avoid the damaging effects of intracellular ice formation. The cryoprotectant in popular use is dimethyl sulphoxide (DMSO), and the use of a controlled rate freezing technique at 1 to 2 °C/min and rapid thawing is considered standard. Passive cooling devices that employ mechanical refrigerators, generally at –80 °C, to cool the cells (so-called dump-freezing) generate cooling rates similar to those adopted in controlled rate freezing. Generally, the outcome from such protocols has been comparable to controlled rate freezing. This has been undertaken to replace the largely empirical approach to developing an optimized protocol with methodology that takes into account the sequence of damaging events occurring during the freezing and thawing process.

A Sterling Cycle Cryocooler has been developed as an alternative to conventional liquid nitrogen controlled rate freezers. Unlike liquid nitrogen systems, the Sterling Cycle freezer does not pose a contamination risk, can be used in sterile conditions and has no need for a constant supply of cryogen. Three types of samples from two species (murine embryos, human spermatozoa and embryonic stem cells), each requiring different cooling protocols, were cryopreserved in the Sterling Cycle freezer. For comparison, cells were also frozen in a conventional liquid nitrogen controlled rate freezer. Upon thawing, the rates of survival of viable cells were generally greater than 50% for mouse embryos and human embryonic stem cells, based on morphology (mouse embryos) and staining and colony formation (human embryonic stem cells). Survival rates of human spermatozoa frozen in the Sterling Cycle freezer, based on motility and dead cell staining, were similar to those of samples frozen in a conventional controlled rate freezer using liquid nitrogen.

HEAT TREATING AND CRYOCOOLING OF METALS

There are many benefits of sub-cooling metals, including:

- Reduces abrasive and adhesive wear. Treated material typically yields two to three times the production of non-treated material
- Permanently changes the structure of the metal resulting in improved machining properties. Treated components may be ground after treatment and the benefits of treatment are retained
- Reduces the frequency and cost of tool remanufacture. Worn treated tools require less material removal to restore a uniform cutting edge. Furthermore treated tools may be reground more times before falling below the minimum acceptable dimensions

- Substantially reduces machine downtime caused by tool replacement
- Improves surface finishing on material being manufactured with treated tooling. Treated tooling stays sharper and in tolerance longer than untreated
- Reduces likelihood of catastrophic tool failures due to stress fracture
- Stress relieves to reduce inherent/residual stress caused by manufacture
- Increases the overall durability of the treated product

Cryogenic processing makes changes to the structure of materials being treated; dependent on the composition of the material it performs three things:

1. Turns retained austenite into martensite
2. Refines the carbide structure
3. Stress relieves

Cryogenic treatment of ferrous metals converts retained austenite to martensite and promotes the precipitation of very fine carbides.

Most heat treatments, at best, will leave somewhere between ten and twenty percent retained austenite in ferrous metals. Because austenite and martensite have different size crystal structures, there will be stresses built into the crystal structure where the two co-exist. Cryogenic processing eliminates these stresses by converting the majority of the retained austenite to martensite.

An important factor to keep in mind is Cryogenic Processing is not a substitute for heat-treating. If the product is poorly treated, cryogenic treatment cannot help it. Also, if the product is overheated during remanufacture or overstressed during use, you may destroy the temper of the steel which is developed during the heat treatment process thus rendering the cryogenic process useless by default. Cryogenic processing will not in itself harden metal like quenching and tempering. It is an additional treatment to heat-treating.

This transformation itself can cause a problem in poorly heat-treated items that have too much retained austenite; it may result in dimensional change and possible stress points in the product being treated. This is why Cryogen Industries will not treat poorly heat-treated items.

The cryogenic metal-treatment process also promotes the precipitation of small carbide particles in tool steels and suitable alloying metals. The fine carbides act as hard areas with a low coefficient of friction in the metal that greatly adds to the wear resistance of the metals.

A Japanese study in the role of carbides in the wear-resistance improvements of tool steel by cryogenic treatment concluded the precipitation of fine carbides has more influence on the wear-resistance increase than does the removal of the retained austenite. The process also relieves residual stresses in

metals and some forms of plastics; this has been proven by field studies conducted on product in high impact scenarios where stress fractures are evident.

Cryogenic Processing is not a coating; it changes the core structure of the material being treated and in reality, works with synergy with coatings. As cryogenics is a once-only treatment you will never wear off the process like a coating, but you will be able to sharpen, dress, or modify your tooling without damaging the process.

Tool Failure - Another good reason to cryogenically treat

Tooling failures that can occur are abrasive and adhesive wear, chipping, deformation, galling, catastrophic failure and stress fracture.

Abrasive wear results from friction between the tool and the work material. Adhesive wear occurs when the action of the tool being used exceeds the material's ductile strength or the material is simply too hard to process.

Adhesive wear causes the formation of micro cracks (stress fractures). These micro cracks eventually interconnect, or network, and form fragments that pull out. This "pullout" looks like excessive abrasive wear on cutting edges when actually they are stress fracture failures. When fragments form, both abrasive and adhesive wear occurs because the fragments become wedged between the tool and the work piece, causing friction. This can then lead to poor finish or at worst, catastrophic tool failure.

Catastrophic tooling failures can cause thousands of dollars in machine damage and production loss. This type of tool failure can cause warping and stress fractures to tool heads and decks as well as rotating and load-bearing assemblies.

LIQUIFICATION OF GASES

Most of the world's Natural Gas resources are remote from the market, and their exploitation is constrained by factors such as transportation costs and market outlets. To increase the economic utilization of Natural Gas, techniques other than pipeline transmission or LNG shipment have been developed. Chemical conversion (liquefaction) of gas to make gas transportable as a liquid and add value to the products is now a proven technology.

HISTORY OF CRYOGENICS:

When we consider the history of cryogenics we see that this technology, like most others, has been evolutionary and not necessarily revolutionary. Steady progress in this technology has brought us to where we are today. The cryogenics industry is flourishing with new applications found every year and for this reason remains tremendously viable and has given us processes that certainly benefit our daily lives.

The Invention

The invention of the thermometer by Galileo in 1592 is considered by some the first step towards establishing the science of thermodynamics. A Galileo thermometer (or Galilean thermometer) is a device made with sealed glass cylinders containing a clear liquid and several additional glass vessels of varying densities. As temperature changes, the individual floats rise or fall in proportion to their respective density. Galileo discovered the principle on which this type of thermometer is based. **That principle being the density of a liquid changes in proportion to its temperature.**

Although named after Galileo, the thermometer described above was not invented by him. Galileo did invent a thermometer, called Galileo's air thermometer (more accurately termed a thermoscope), in or before the year 1603. The so-called 'Galileo thermometer' was actually invented by a group of academics and technicians known as the Accademia del Cimento of Florence. This group included one of Galileo's pupils, Evangelista Torricelli and Torricelli's pupil, Viviani. **Torricelli** was an Italian physicist and mathematician, best known for his invention of the barometer even though he contributed to inventing the thermometer. Details of the thermometer were published in the *Saggi di naturali esperienze fatte nell'Accademia del Cimento sotto la protezione del Serenissimo Principe Leopoldo di Toscan e descrittadel segretario di essa Accademia* (1666), the Academy's main publication. The English translation of this work (1684) describes the device ('The Fifth Thermometer') as 'slow and lazy', a description that is reflected in an alternative Italian name for the invention, the *termometro lento* (slow thermometer). The outer vessel was filled with 'rectified spirits of wine' (a concentrated solution of ethanol in water), the weights of the glass bubbles were adjusted by grinding a small amount of glass from the sealed end, and a small air space was left at the top of the main vessel to allow 'for the Liquor to rarefie'.

Guillaume Amontons actually predicted for the first time the existence of an absolute zero in 1702. Some say this prediction marked the beginning of the science of low temperatures. Around 1780, the liquefaction of a gas was achieved for the first time. It took almost 100 years before a so-called "permanent" gas, i.e. oxygen, was successfully liquefied. Thereafter, Linde and Claude founded the cryogenic industry, which today has annual sales of more than 30 billion US \$. Kamerlingh Onnes and his Cryogenic Laboratory in Leiden worked in the field of low temperature physics, which contributed to the experimental proof of the quantum theory. Heike Kamerlingh Onnes (1853-1926; 1913 Nobel Prize winner for physics) liquefied the most difficult gas of all, helium. He liquefied that gas at the lowest temperature ever achieved in a laboratory to that date, 4.2 Kelvin (the Kelvin measurement is a scale of temperatures measured in degrees Celsius from absolute zero). We will discuss the Kelvin temperature scale in depth later on in this course. This marked a significant milestone in the history of cryogenics. Since that achievement, increased attention has been devoted to the study of physical phenomena of substances at very low temperatures.

Early Research

British chemists Michael Faraday (1791-1867) and Sir Humphry Davy (1778-1829) did pioneering work in low-temperature physics that led to the ongoing development of cryogenics. In the early to middle 1800s they were able to produce gases by heating mixtures at one end of a sealed tube in the shape of an inverted "V." A salt and ice mixture was used to cool the other end of the tube. This combination of

reduced temperature and increased pressure caused the gas that was produced to liquefy (turn to a liquid). When they opened the tube, the liquid quickly evaporated and cooled to its normal boiling point.

In 1877, French mining engineer Louis Paul Cailletet announced that he had liquefied oxygen and nitrogen. Cailletet was able to produce only a few droplets of these liquefied gases, however. In his research with oxygen, Cailletet collected the oxygen in a sturdy container and cooled it by evaporating sulphur dioxide in contact with the container. He then compressed the oxygen as much as possible with his equipment. Next he reduced the pressure suddenly, causing the oxygen to expand. The sudden cooling that resulted caused a few drops of liquid oxygen to form.

The need to store liquefied gases led to another important development in cryogenics. In 1891 Scottish chemist James Dewar (1842-1923) introduced the container known today as the "Dewar flask." The Dewar flask is actually two flasks, one within the other, separated by an evacuated space (a vacuum). The inside of the outer flask and the outside of the inner flask are coated with silver. The vacuum and the silvered sides of the container are designed to prevent heat passage.

Dewar was also the first person to liquefy hydrogen in 1898. Cryogenics, as we recognize it today, started in the late 1800's when Sir James Dewar (1842 – 1923) perfected a technique for compressing and storing gases from the atmosphere into liquids. (Some credit a Belgian team as being first to separate and liquefy gases, but being British we'll stay with Sir James Dewar for now). These compressed gases were super cold, and any metal that came in contact with the ultra low temperatures showed some interesting changes in their characteristics.



The first liquefied hydrogen by Sir James was in 1898, and a year later he managed to solidify hydrogen – just think on that for a moment... This is before electricity was common in houses, cars and buses a rare find and photography a rich man's hobby. By pure persistence and fantastic mental ability a whole generation of 'Gentleman Scientists' managed to bring into existence many things we both rely on and take for granted today.

Sir James managed to study, and lay the cornerstones for the production of a wide range of gases that we use in our everyday lives, mostly without even realizing it. He also invented the Thermos flask (how else was he to save his liquid gas samples), the industrial version of which still uses his name - 'Dewar'?

Later Accomplishments

In the 1940's, scientists discovered that by immersing specific metals in liquid nitrogen, they could increase the wear resistance of motor parts, particularly in aircraft engines, giving a longer in-service life. At the time this was little more than dipping a part into a flask of liquid nitrogen, leaving it there for an hour or two and then letting it return to room temperature. They managed to get the hardness they

wanted, but parts became brittle. As some benefits could be found in this crude method, further research into the process was conducted. The applications at this stage were mostly military.

NASA led the way and perfected a method to gain the best results, consistently, for a whole range of metals. The performance increase in parts was significant, but so was the cost of performing the process.

Work continued over the years to perfect the process, insulation materials improved, the method of moving the gas around the process developed and, most importantly, the ability to tightly control the rate of temperature change.

Technology enabled scientists to look deeper into the very structure of metals and better understand what was happening to the atoms and how they bond with other carbons. They also started to better understand the role that temperature plays in the treatment of metals to effect the final characteristics (more information in the 'How it works' section).

As with most everything in our lives today, the microprocessor enabled a steady but continual reduction in size of the control equipment required as well as increasing the accuracy of that part of the process.

Since the mid 1990's, the process has started to become a commercially viable treatment in terms of cost of process vs. benefits in performance.

TEMPERATURE SCALES:

I think before we go further with technical descriptions of the cryogenic process, it is absolutely necessary that we discuss temperature scales. There are basically four (4) scales used in science, technology and industry today. These are: 1.) Fahrenheit 2.) Celsius, 3.) Rankin and 4.) Kelvin.

FAHRENHEIT SCALE

Fahrenheit temperature scale is a scale based on 32 for the freezing point of water and 212 for the boiling point of water, the interval between the two being divided into 180 parts. The 18th-century German physicist Daniel Gabriel Fahrenheit originally took as the zero of his scale the temperature of an equal ice-salt mixture and selected the values of 30 and 90 for the freezing point of water and normal body temperature, respectively; these later were revised to 32 and 96, but the final scale required an adjustment to 98.6 for the latter value.

Until the 1970s the Fahrenheit temperature scale was in general common use in English-speaking countries; the Celsius, or centigrade, scale was employed in most other countries and for scientific purposes worldwide. Since that time, however, most English-speaking countries have officially adopted the Celsius scale. The conversion formula for a temperature that is expressed on the Celsius (C) scale to its Fahrenheit (F) representation is: $F = 9/5C + 32$.

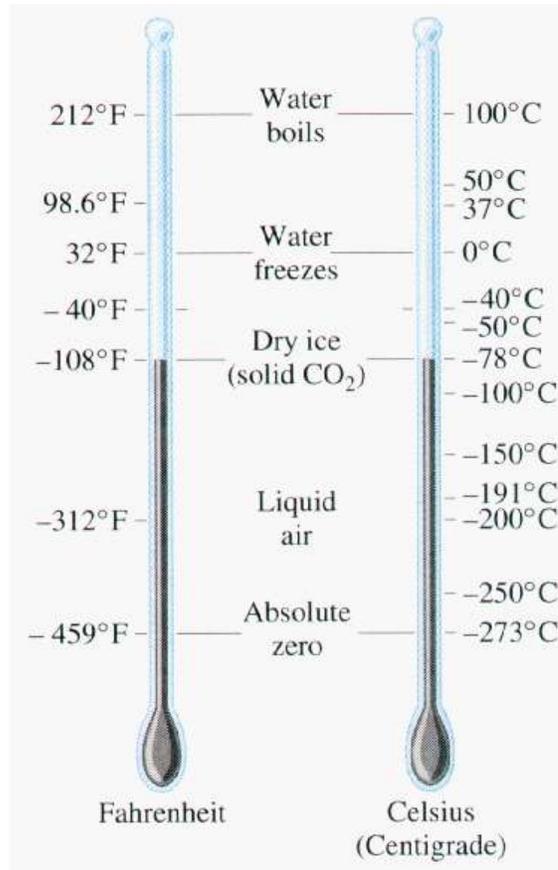


FIGURE 2: COMPARISON BETWEEN FAHRENHEIT AND CELSIUS

CELSIUS SCALE

Celsius temperature scale, also called centigrade temperature scale, is the scale based on 0 for the freezing point of water and 100 for the boiling point of water. Invented in 1742 by the Swedish astronomer, Anders Celsius, it is sometimes called the centigrade scale because of the 100-degree interval between the defined points. The following formula can be used to convert a temperature from its representation on the Fahrenheit (F) scale to the Celsius (C) value: $C = 5/9(F - 32)$. The Celsius scale is in general use wherever metric units have become accepted, and it is used in scientific work everywhere.

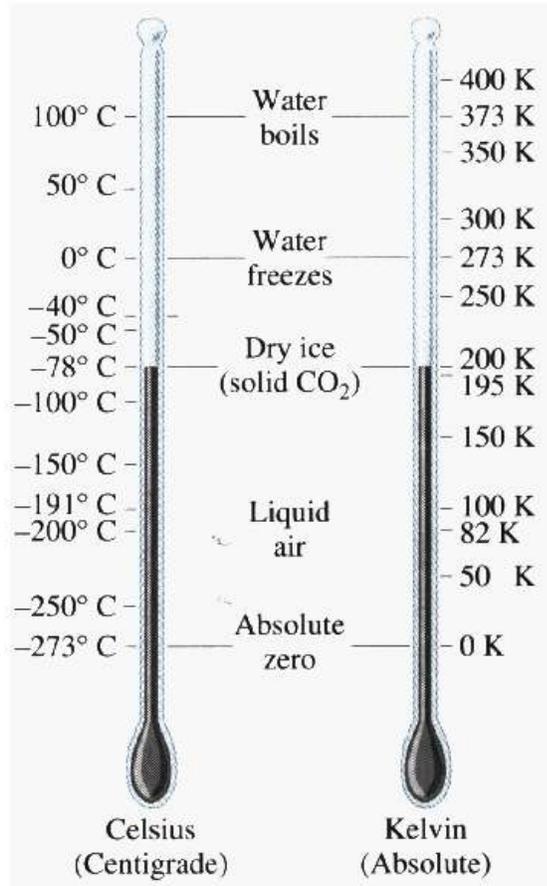


FIGURE 3: COMPARISON BETWEEN CELSIUS AND KELVIN

KELVIN SCALE

Lord Kelvin was a Scottish mathematician and physicist who contributed to many branches of physics. He was known for his self-confidence, and as an undergraduate at Cambridge he thought himself the sure "Senior Wrangler" (the name given to the student who scored highest on the Cambridge mathematical Tripos exam). After taking the exam he asked his servant, "Oh, just run down to the Senate House, will you, and see who is Second Wrangler." The servant returned and informed him, "You, sir! Another example of his hubris is provided by his 1895 statement "heavier-than-air flying machines are impossible" (Australian Institute of Physics), followed by his 1896 statement, "I have not the smallest molecule of faith in aerial navigation other than ballooning...I would not care to be a member of the Aeronautical Society." Kelvin is also known for an address to an assemblage of physicists at the British Association for the advancement of Science in 1900 in which he stated, "There is nothing new to be discovered in physics now. All that remains is more and more precise measurement." A similar statement is attributed to the American physicist Albert Michelson

Kelvin temperature scale is the base unit of thermodynamic temperature measurement in the International System (SI) of measurement. It is defined as 1/ 273.16 of the triple point (equilibrium among the solid, liquid, and gaseous phases) of pure water. The Kelvin (symbol K without the degree sign) is also the fundamental unit of the Kelvin scale, an absolute temperature scale named for the British physicist William Thomson, Baron Kelvin. Such a scale has as its zero point absolute zero, the theoretical temperature at which the molecules of a substance have the lowest energy. Many physical laws and formulas can be expressed more simply when an absolute temperature scale is used; accordingly, the Kelvin scale has been adopted as the international standard for scientific temperature measurement. The Kelvin scale is related to the Celsius scale. The difference between the freezing and boiling points of water is 100 degrees in each, so that the Kelvin has the same magnitude as the degree Celsius.

The following table giving the mathematical conversions may be seen comparing the various temperature scales relative to the Kelvin scale

Kelvin temperature conversion formulae

	from Kelvin	to Kelvin
Celsius	$[^{\circ}\text{C}] = [\text{K}] - 273.15$	$[\text{K}] = [^{\circ}\text{C}] + 273.15$
Fahrenheit	$[^{\circ}\text{F}] = [\text{K}] \times \frac{9}{5} - 459.67$	$[\text{K}] = ([^{\circ}\text{F}] + 459.67) \times \frac{5}{9}$
Rankine	$[^{\circ}\text{R}] = [\text{K}] \times \frac{9}{5}$	$[\text{K}] = [^{\circ}\text{R}] \times \frac{5}{9}$
For temperature <i>intervals</i> rather than specific temperatures, $1 \text{ K} = 1 ^{\circ}\text{C} = \frac{9}{5} ^{\circ}\text{F} = \frac{9}{5} ^{\circ}\text{R}$ <i>Comparisons among various temperature scales</i>		

TABLE 2: CONVERSION FORMULA

Thomson also calculated the age of the earth from its cooling rate and concluded that it was too short to fit with Lyell's theory of gradual geological change or Charles Darwin's theory of the evolution of animals through natural selection. He used the field concept to explain electromagnetic interactions. He speculated that electromagnetic forces were propagated as linear and rotational strains in an elastic solid, producing "vortex atoms" which generated the field. He proposed that these atoms consisted of tiny knotted strings, and the type of knot determined the type of atom. This led Tait to study the properties of knots. Kelvin's theory said ether behaved like an elastic solid when light waves propagated through it. He equated ether with the cellular structure of minute gyrostats. With Tait, Kelvin published *Treatise on Natural Philosophy* (1867), which was important for establishing energy within the structure of the theory of mechanics. (It was later republished under the title *Principles of Mechanics and Dynamics* by Dover Publications).

A picture of Lord Kelvin is shown below:



FIGURE 4: LORD KELVIN

RANKINE SCALE:

Rankine is a thermodynamic (absolute) temperature scale named after the Glasgow University engineer and physicist William John Macquorn Rankine, who proposed it in 1859.

The symbol for **degrees Rankine** is °R (or °Ra if necessary to distinguish it from the Rømer and Réaumur scales). Zero on both the Kelvin and Rankine scales is absolute zero, but the Rankine degree is defined as equal to one degree Fahrenheit, rather than the one degree Celsius used by the Kelvin scale. A temperature of $-459.67\text{ }^{\circ}\text{F}$ is exactly equal to $0\text{ }^{\circ}\text{R}$.

Some engineering fields in the U.S. measure thermodynamic temperature using the Rankine scale. In the scientific world, thermodynamic temperature is usually measured using the Kelvin scale. The US National Institute of Standards and Technology recommends not using degrees Rankine in NIST publications.

Key temperatures relating the Rankine scale to other temperature scales for various substances are shown in the table below.

	Kelvin	Celsius	Fahrenheit	Rankine
Absolute zero (by definition)	0 K	-273.15 °C	-459.67 °F	0 °R
Freezing point of brine (by definition on Fahrenheit scale(only))	255.37 K	-17.78 °C	0 °F	459.67 °R
Freezing point of water	273.15 K	0 °C	32 °F	491.67 °R
Triple point of water (by definition)	273.16 K	0.01 °C	32.018 °F	491.688 °R
Boiling point of water	373.1339 K	99.9839 °C	211.97102 °F	671.64102 °R

TABLE 3: COMPARISON BETWEEN THE FOUR TEMPERATURE SCALES

SAFETY MEASURES WHEN HANDLING CRYOGENIC MATERIALS

The placement of safety measures may be somewhat odd at this point, but I now wish to indicate several safety issues that you will be faced with when dealing with cryogenic liquids and materials. **IT IS VITAL** to acknowledge that specific measures **MUST** be taken when working with fluids and materials approaching absolute zero. **THIS IS BIG- AND WHEN DEALING WITH CRYOGENIC PROCESSES AND MATERIALS—SAFETY CANNOT BE IGNORED!!**

HAZARDS

Let us first look at the hazards in dealing with cryogenic materials. These are as follows:

There are three groups of health hazards associated with cryogenic liquids: extreme cold, asphyxiation, and toxicity.

Extreme Cold Hazard

Cryogenic liquids and their associated cold vapors and gases can produce effects on the skin similar to a thermal burn. Brief exposures that would not affect skin on the face or hands can damage delicate tissues such as the eyes. Prolonged exposure of the skin or contact with cold surfaces can cause frostbite. The skin appears waxy yellow. There is no initial pain, but there is intense pain when frozen tissue thaws.

Unprotected skin can stick to metal that is cooled by cryogenic liquids. The skin can then tear when pulled away. Even non-metallic materials are dangerous to touch at low temperatures. Prolonged breathing of extremely cold air may damage the lungs.

Asphyxiation Hazard

When cryogenic liquids form a gas, the gas is very cold and usually heavier than air. This cold, heavy gas does not disperse very well and can accumulate near the floor. Even if the gas is non-toxic, it displaces air. When there is not enough air or oxygen, asphyxiation and death can occur. Oxygen deficiency is a serious hazard in enclosed or confined spaces.

Small amounts of liquid can evaporate into very large volumes of gas. For example, one liter of liquid nitrogen vaporizes to 695 liters of nitrogen gas when warmed to room temperature (21°C).

Toxic Hazards

Each gas can cause specific health effects. For example, liquid carbon monoxide can release large quantities of carbon monoxide gas, which can cause death almost immediately. Refer to the material safety data sheet for information about the toxic hazards of a particular cryogen.

What are the flammability hazards of cryogenic liquids?

Several types of situations exist that may result in a flammability hazard including: fire, oxygen-enriched air, liquid oxygen, and explosion due to rapid expansion.

Fire Hazard

Flammable gases such as hydrogen, methane, liquefied natural gas and carbon monoxide can burn or explode. Hydrogen is particularly hazardous. It forms flammable mixtures with air over a wide range of concentration (4 percent to 75 percent by volume). It is also very easily ignited.

Oxygen-Enriched Air

Liquid hydrogen and liquid helium are both so cold that they can liquefy the air they contact. For example, liquid air can condense on a surface cooled by liquid hydrogen or helium. Nitrogen evaporates more rapidly than oxygen from the liquid air. This action leaves behind a liquid air mixture which, when evaporated, gives a high concentration of oxygen. This oxygen-enriched air now presents all of the same hazards as oxygen.

Liquid Oxygen Hazard

Liquid oxygen contains 4,000 times more oxygen by volume than normal air. Materials that are usually considered non-combustible, (such as carbon and stainless steels, cast iron, aluminum, zinc and Teflon (PTFE),) may burn in the presence of liquid oxygen. Many organic materials can react explosively, especially if a flammable mixture is produced. Clothing splashed or soaked with liquid oxygen can remain highly flammable for hours.

Explosion Due to Rapid Expansion

Without adequate venting or pressure-relief devices on the containers, enormous pressures can build up. The pressure can cause an explosion called a "boiling liquid expanding vapor explosion" (BLEVE).

Unusual or accidental conditions such as an external fire, or a break in the vacuum which provides thermal insulation, may cause a very rapid pressure rise. The pressure relief valve may not be able to handle this increased pressure. Therefore, the containers must also have another backup device such as a frangible (bursting) disc.

SUBSTITUTION FOR CRYOGENIC MATERIALS

Substitution is often the best way to avoid or reduce a hazard. But it is not always easy or even possible to find a less hazardous substitute for a particular cryogenic liquid used for a specific job. Chemical suppliers may be able to suggest possible safer substitutes to meet the specific needs of your workplace.

Obtain MSDSs for all possible substitutes. Find out about all of the hazards (health, fire, chemical reactivity) of these materials before making any substitutions. Choose the least hazardous material.

VENTILATION

Well-designed and maintained ventilation systems remove gases from the workplace and reduce their hazards. To reduce the risk of fire, explosion or asphyxiation, ensure proper ventilation where cryogenics are stored or used.

The amount and type of ventilation needed depends on such factors as the type of job, the kind and amount of materials used, and the size and layout of the work area. Some workplaces may need a complete system of hoods and ducts to provide acceptable ventilation. Others may require a single, well-placed exhaust fan. No special ventilation system may be needed where small amounts of inert gases are used. Assess the specific ways cryogenic liquids are stored, handled, used and disposed of in the workplace to find out if existing ventilation controls (and other hazard control methods) are adequate.

Make sure ventilation systems are designed and built so they do not result in an unintended hazard. Ensure hoods, ducts, air cleaners and fans are made from materials compatible with the gas used. Explosion-proof equipment may be required.

Separate ventilation systems may be needed to keep some cryogenic liquids away from systems exhausting incompatible substances.

STORING CRYOGENIC LIQUIDS

Inspect all incoming containers before storing to ensure they are not damaged and are properly labeled. Do not accept delivery of defective containers. Always use the correct name for all materials. For example, never call liquid oxygen "liquid air". If the oxygen is available in a mixture, refer to it as "medium purity liquid oxygen" or "oxygen mixture". Handle any mixtures with an oxygen concentration greater than air with the same precautions as pure liquid oxygen.

Keep Dewar flasks covered with a loose fitting cap. This method prevents air or moisture from entering the container, yet allows pressure to escape. Use only the stopper or plug supplied with the container. Glass Dewar flasks are available, but never use them to store combustible or oxidizing cryogenic liquids. Put tape on glass Dewar flasks. The tape will minimize any hazards from flying glass should the flask fracture when a cryogenic liquid is poured into it.

Ensure that ice does not form in the neck of flasks. Liquids such as helium and hydrogen can freeze the water vapor in the surrounding air which can create a pressure hazard. Dewar flasks are not pressure vessels so if the opening is blocked pressure can slowly build up. Eventually, the pressure may cause a violent rupture. If the neck of the Dewar flask is blocked by ice or "frozen" air, follow the manufacturer's instruction for removing it. Ice can also cause pressure relief valves to malfunction or become blocked.

Do not store containers where they may come into contact with moisture. Moving parts, such as valves or pressure-relief devices, can malfunction due to external ice formation.

Ensure that ignition sources and combustible materials are kept far away from liquefied oxygen and other flammable material storage and handling areas. Ensure that vessels are insulated from any sources of heat.

Do not store liquid oxygen containers on wood, asphalt or oil-soaked gravel. When saturated with liquid oxygen, these materials have exploded after an impact as slight as a footstep. Use concrete or clean gravel under storage areas.

Store all cryogenic liquid containers upright in well-ventilated areas. Handle them carefully, and avoid dropping, rolling or tipping them on their sides. Take the same precautions for storing liquid cryogenes as are needed for storing these materials in their gas form.

Use care when loading or unloading by forklift, crane or other power-assist devices. Always ensure the container is secure to pallet or a similar device.

Restrict access to storage areas. Allow only authorized people into the storage areas. Clearly post warning signs and emergency instructions.

TRANSPORTING CRYOGENIC LIQUIDS

Move cryogenic liquid containers carefully. Do not move a container by rolling it on its lower rim. Always use a hand truck, cart, or other proper handling device. Use a strap to secure the container to the handcart. Keep the cryogenic liquid containers upright at all times except for the minor tilting on the cart during transport. Always push the container (don't pull) as pushing reduces the chance of the container falling on you or a co-worker. If cryogenes must be transported by elevator, take adequate precautions to prevent possible injury. Send cryogenic liquids in elevators without any passengers and ensure that no passengers get on the elevator while the cryogen is being transported. If a power failure

occurred, a passenger would be trapped in the confined space of an elevator with the cryogen. Excessive amounts of the cryogen could vaporize and displace the oxygen.

HANDLING CRYOGENIC LIQUIDS

Only handle cryogenic liquids if you are fully aware of the properties of the materials and the equipment. Written procedures and checklists should be developed. Changes in procedures should only be allowed after a proper review and if necessary, consultation with the supplier. For particularly hazardous operations, a work permit system should be put into place. A competent person should examine all the equipment and review the proposed procedures before the work begins.

SELECTING MATERIALS USED WITH CRYOGENS

At the extremely low temperatures of cryogenic liquids, many common materials such as carbon steel, plastics and rubber become brittle and can crack. This process is called "embrittlement" (e.g. Do not pour cryogenics down the drain). Many materials also shrink at cryogenic temperatures, potentially causing leaks at hose connections. Therefore, take care when selecting materials to be used with cryogens. Regardless of the materials chosen, do not allow water to contaminate equipment. Freezing ice will expand and can crack equipment.

Cooling Operations

When using cryogenic liquids to cool an object, insert the object SLOWLY using tongs. This procedure minimizes any boiling and splashing which occurs when warm objects are added rapidly. Never wear watches, rings, bracelets or other jewelry, because, if splashed by a cryogen, they can freeze to exposed skin.

TRANSFERRING CRYOGENIC LIQUIDS

When transferring cryogenic liquids from one container to another, cool the receiving Dewar flask before filling it. Always start filling slowly to allow the vaporization to chill the receiving container. After the vaporization and liquid boiling has decreased, fill the container at the normal rate. Devices which reduce turbulence while filling are available for attachment to your transfer hose. These attachments will significantly reduce the release of gas. Contact your gas supplier for information.

When pouring cryogenic liquids, use an appropriate filling device. For wide-mouthed containers, this may be a funnel. When it is not safe or convenient to tilt the container, use a discharge tube to remove the liquid. Insert the discharge tube through the neck of the container and well down into the liquid. The packing material or stopper on the discharge tube should form a seal in the neck of the container. Normal evaporation usually produces enough pressure to push liquid out. If necessary, the container may be pressurized with the same gas as the liquid or with an oil-free inert gas. Use just enough pressure to force liquid out. Never fill containers higher than the indicated level.

Fill containers only with liquids they are designed to hold. Mixing flammable cryogenics and liquid oxygen produces a fire hazard. If liquid oxygen is used in a liquid nitrogen refrigerator, any organic materials in the refrigerator could burst into flames.

HOW TO HANDLE LIQUID OXYGEN

Prevent all organic substances including oils and greases from contacting liquid oxygen. Thoroughly clean any equipment or container used with liquid oxygen to the degree required for use with oxidizing materials. Some common materials (such as asphalt kerosene, cloth, wood, paint, tar, and dirt containing oil or grease) can react violently with liquid oxygen at certain pressures and temperatures.

Immediately remove clothing that is splashed with liquid oxygen and air it out for at least one hour. If a fire starts in an area where liquid oxygen is flowing, stop the flow of oxygen. Do not allow smoking or open flames in any area where liquid oxygen is stored, handled or used.

HOW TO HANDLE LIQUID HYDROGEN

Liquid hydrogen is a severe fire hazard because it is easily ignited, has a wide flammable temperature range, and produces a colorless flame that is difficult to see. Therefore, limit the amount of liquid hydrogen used indoors.

Simply opening a hydrogen container can produce enough energy to start the gas burning. In fighting a hydrogen fire, it is important to first stop or turn off the flow of hydrogen gas. Simply smothering or blowing out the flame without shutting off the hydrogen supply can create an explosion hazard. If the hydrogen supply cannot be turned off, it may be best to let the fire burn. Control the spread of the fire until the fuel is used up.

SPECIAL TRAINING

Anyone who handles, stores or transfers cryogenic liquids requires instruction on safe-handling practices. Specific areas of instruction should include:

- properties of the cryogen both as a liquid and as a gas
- specific instructions on the equipment being used, including safety devices
- approved materials that are compatible with the cryogen
- selection, use and care of protective equipment and clothing
- first aid, including self-treatment
- dealing with emergencies such as fires, leaks and spills

- good housekeeping practices

GOOD HOUSEKEEPING

Maintain good housekeeping at all times in the workplace.

- Do not contaminate cryogenic liquids or their containers.
- Never allow combustible organic materials near liquid oxygen.
- Prevent mixing of flammable and oxidizing cryogens.
- Never allow any absorbent materials to be exposed to flammable or oxidizing cryogens.
- When venting storage containers, proper consideration must be given to all the properties of the gas being vented. Venting should be to the outdoors with appropriate environmental considerations. This prevents the accumulation of flammable, toxic, oxidizing or inert gases in the work area.

PERSONAL CLEANLINESS

Personal cleanliness helps protect people working with hazardous materials. (This is particularly important with liquid oxygen).

- Remove contaminated clothing since it may be a severe fire or health hazard.
- Do not wear or carry items contaminated with oxidizing or flammable cryogens into areas with ignition sources or where smoking is allowed.
- Do not store food and tobacco products in work areas.
- Wash hands before eating, drinking, smoking or going to the toilet.
- Wash yourself thoroughly at the end of the workday.

PROPER MAINTENANCE

- Regular equipment maintenance can prevent hazardous conditions in the workplace.
- Always follow all the manufacturer's procedures for operating and maintaining equipment used with cryogens.
- Comply with applicable regulations and follow the advice of the cryogenic liquid supplier.
- Repair equipment properly, using tools and procedures suitable for the contents of the cryogenic liquid container.

- Avoid forcing connections, using homemade adaptors, or tampering with containers in any way.
- When doing maintenance work on oxygen-handling systems, cleanliness is required. Grease or oil must not be allowed to contaminate any parts.

Regular workplace inspections can help to spot situations in which cryogenic liquids are stored, handled or used in potentially hazardous ways.

PERSONAL PROTECTIVE EQUIPMENT (PPE)

It is essential to choose the right personal protective equipment (PPE) for a particular job. MSDSs should provide general guidance. Also obtain advice from someone who knows how to evaluate the hazards of the job and how to select the proper PPE.

Avoid Skin Contact

Cryogenic liquids flow very freely and can penetrate woven or other porous clothing much faster than water. Wear a non-porous, knee-length laboratory coat, without pockets or cuffs which could catch the liquid. If using larger quantities of cryogenic liquids, wear an apron of a non-woven material such as leather. Wear boots with tops high enough to be covered by pants without cuffs. Wear loose fitting, insulated gloves when handling anything that may have been in contact with a cryogenic liquid. The gloves must be loose so they can be thrown off quickly if liquid spills into them. Insulated welding gloves are one type of glove that has been found useful.

Use tongs or proper gloves to handle objects that are in contact with cryogenic liquids.

Protect Your Eyes and Face

Wear safety glasses whenever you are near a cryogenic liquid. Protect the eyes with a full-face shield if a cryogenic liquid is poured or if an open container of the cryogen may bubble. The CSA Standard Z94.3 "Eye and Face Protectors", provides advice on selection and use of eye and face protectors.

Avoid Breathing Harmful Gases

If respirators must be used for breathing protection, develop and follow a written respiratory protection program. The CSA Standard Z94.4, "Selection, Care and Use of Respirators," gives guidance for developing a program. Follow all legal requirements for respirator use and approvals. These requirements may vary between jurisdictions in Canada.

Remember, air-purifying respirators do not protect against oxygen-deficient environments. In situations where low oxygen levels occur, use supplied air or self-contained breathing apparatus.

Be familiar with the right PPE for use in emergencies as well as during normal operations.

Wear the PPE needed for doing a particular job. It cannot provide protection if it is not worn.

FIRST AID MEASURES WHEN NEEDED

Avoid contact with cryogenic liquids, their vapors and any cooled surfaces. If contact does occur, immediately flush the area with large quantities of warm (not hot) water. If the skin is blistered or the eyes have been exposed, obtain medical attention immediately. Locate emergency eyewash stations and safety showers wherever there may be accidental exposures to cryogenes.

EMERGENCY PROCEDURES

Prepare for emergencies. Planning, training and practicing help people to know what they must do. The MSDSs are a starting point for drawing up an emergency plan. MSDSs have specific sections on spill and leak procedures, first aid instructions, and fire and explosion hazards. If the directions in each MSDS section are not clear or seem incomplete, contact the cryogen supplier or manufacturer for help.

Many other sources can also help develop emergency plans. Local fire departments can assist with fire emergency plans and training. Occupational health and safety and environmental regulatory agencies, provincial safety associations, the Canadian branch of the Compressed Gas Association, St. John Ambulance, insurance carriers, professional societies in occupational health and safety, labor unions, some colleges and universities, and CCOHS can supply useful information. Specialized private consultants are also available. All major suppliers in Canada have emergency response plans in place. Make sure you know the response number provided by your supplier.

Act quickly in emergencies such as chemical fires or cryogenic vessel leaks.

- Evacuate the area at once if you are not trained to handle the problem or if it is clearly beyond your control.
- Alert other people in the area to the emergency.
- Call the fire department immediately.
- Report the problem to the people responsible for handling emergencies where you work.
- Obtain first aid if you have been exposed to harmful chemicals.

Remove all contaminated clothes.

Only specially trained and properly equipped people should handle emergencies. Nobody else should go near the area until it is safe.

If a liquid oxygen container falls over, evacuate the area and observe the container from a safe position for 30 minutes. If the inner vessel is damaged, a leak could cause an ignition in the insulation space when the vessel is moved. Contact your supplier immediately if the inner vessel of a liquid oxygen container is damaged.

Cryogenics can be particularly dangerous during fires. Cryogenic liquids can freeze water very rapidly. Careless use of water can lead to heavy icing, possibly blocking pressure relief valves. The relatively warm water can also cause a flammable cryogenic liquid to vaporize more rapidly. This rapid evaporation produces more flammable gas to feed the fire.

BEST PRACTICES WHEN WORKING WITH CRYOGENIC LIQUIDS

Following these basic general safe practices will help protect you from the hazards of cryogenic liquids:

- Read the MSDSs and labels for all of the materials you work with.
- Know all of the hazards (fire/explosion, health, chemical reactivity, pressure) of the materials you work with.
- Store cryogen containers in cool, dry, well-ventilated areas, away from incompatible materials and ignition sources.
- Store, handle and use cryogen containers securely fastened in place in the upright position.
- Ensure that pressure relief valves are working properly.
- Never tamper with safety devices on vessels, valves or equipment.
- Never roll, drag, or drop vessels or permit them to strike each other.
- Move containers in handcarts or other devices designed for moving cryogenic liquid vessels
- Ensure proper ventilation in areas where cryogenics are stored or used to reduce the risk of fire, explosion or asphyxiation.
- Fill containers only with the liquids for which they were designed. Label each container. Fill vessels to the indicated level only. Do not overfill.
- Proceed slowly when filling a container or inserting objects into a cryogen to minimize boiling and splashing.
- Prevent frostbite by never allowing cryogenic liquids to touch your skin.
- Never wear watches, rings, bracelets, or other jewelry that could freeze to your skin.
- Always wear loose fitting insulated gloves when handling anything that may have been in contact with a cryogen.
- Wear safety glasses whenever you are near a cryogen, and a face shield when pouring a cryogen.
- Wear the proper personal protective equipment for each of the jobs you do.

- Know the location of eyewash stations and safety showers.
- Obtain proper training on how to use all of the materials and equipment you are using.
- Know how to deal with emergencies (fires, leaks, personal injury).
- Follow the health and safety rules that apply to your job.

IN SUMMARY

- **Engineering controls**
 - Enclosed systems
 - Natural or forced ventilation
 - Use a liquid nitrogen pump to decant the substance rather than pouring
 - Use of equipment designed for use with cryogenic fluids
 - Inspection and maintenance program to ensure dewars, cylinders and equipment are in good condition
 - Low oxygen alarms
 - Interlocking doors
 - Emergency equipment, such as safety shower and eye wash unit
- **Administrative controls**
 - Training of persons using liquid nitrogen
 - Safe working procedures
 - Supervision and never work alone
 - Limited access to hazardous areas
 - Emergency response procedure
 - Good housekeeping
 - Good personal hygiene
- **Selection and use of personal protective equipment**
 - Full face shield;

- Clean and dry cryogenic gloves for handling cold items or thick leather gloves to protect against splashes and for handling cold items (gloves should be loose fitting and easy to slip off in the event of a spill which enters the glove)
- Closed-in footwear that can be removed easily in the event of a spill
- Long pants should be worn (on the outside of footwear)
- Air-supplied breathing apparatus will be needed for work in an oxygen deficient atmosphere (i.e. less than 18%).

PROPERTIES OF GASES USED FOR CRYOGENIC PURPOSES:

What are cryogenic liquids?

Cryogenic liquids are liquefied gases that are kept in their liquid state at very low temperatures. The word "cryogenic" means "producing, or related to, low temperatures," and all cryogenic liquids are extremely cold. Cryogenic liquids have boiling points below -150°C (-238°F) (Carbon dioxide and nitrous oxide, which have slightly higher boiling points are sometimes included in this category). All cryogenic liquids are gases at normal temperatures and pressures. These gases must be cooled below room temperature before an increase in pressure can liquefy them. Different cryogens become liquids under different conditions of temperature and pressure, but all have two properties in common: they are extremely cold, and small amounts of liquid can expand into very large volumes of gas.

The vapors and gases released from cryogenic liquids also remain very cold. They often condense the moisture in air, creating a highly visible fog. In poorly insulated containers, some cryogenic liquids actually condense the surrounding air, forming a liquid air mixture. Cryogenic liquids are classified as "compressed gases" according to WHMIS criteria. Details of these criteria can be found in the Controlled Products Regulations.

What are the different types of cryogenic liquids?

Each cryogenic liquid has its own specific properties but most cryogenic liquids can be placed into one of three groups:

- **Inert Gases:** Inert gases do not react chemically to any great extent. They do not burn or support combustion. Examples of this group are nitrogen, helium, neon, argon and krypton.
- **Flammable Gases:** Some cryogenic liquids produce a gas that can burn in air. The most common examples are hydrogen, methane and liquefied natural gas.
- **Oxygen:** Many materials considered as non-combustible can burn in the presence of liquid oxygen. Organic materials can react explosively with liquid oxygen. The hazards and handling precautions of liquid oxygen must therefore be considered separately from other cryogenic liquids.

PERMANENT GASES

The common permanent gases change from gas to liquid at atmospheric pressure at the temperatures shown below, called the normal boiling point (NBP). Such liquids are known as cryogenic liquids or cryogenes. When liquid helium is cooled further to 2.17 K or below, it becomes a super-fluid with very unusual properties associated with being in the quantum mechanical ground state. For example, it has zero viscosity and produces a film that can creep up and over the walls of an open container, such as a beaker, and drip off the bottom as long as the temperature of the container remains below 2.17 K.

Cryogen	(K)	(°C)	(°R)	(°F)
Methane	111.7	-161.5	201.1	-258.6
Oxygen	90.2	-183.0	162.4	-297.3
Nitrogen	77.4	-195.8	139.3	-320.4
Hydrogen	20.3	-252.9	36.5	-423.2
Helium	4.2	-269.0	7.6	-452.1
Absolute zero	0	-273.15	0	-459.67

TABLE 4: PROPERTIES OF GASES VS CRYO-TEMPERATURES

One other table describing cryo-properties of gases may be seen as follows:

Gas	Helium - He -	Hydrogen - H ₂ -	Methane - CH ₄ -	Nitrogen - N ₂ -	Oxygen - O ₂ -	Fluorine - F ₂ -
Density at Normal Pressure and Temperature - NPT (lb/ft ³)	0.0103	0.0052	0.0415	0.0724	0.0827	0.0982
Boiling point at 1 atm (°F)	-452.1	-423.2	-258.2	-320.4	-297.4	-306.6
Vapor density at boiling point (lb/ft ³)	1.06	0.084	0.111	0.288	0.296	
Liquid density at boiling point (lb/ft ³)	7.62	4.37	26.46	50.41	71.27	94.2

Gas	Helium - He -	Hydrogen - H ₂ -	Methane - CH ₄ -	Nitrogen - N ₂ -	Oxygen - O ₂ -	Fluorine - F ₂ -
Heat of vaporization (Btu/lb)	8.8	193	219.2	85.2	91.7	74.1
Critical Temperature (°F)	-450.3	-400.3	-116.5	-232.8	-181.1	-200.2
Critical Pressure (psia)	33.2	187.7	673.1	492.3	736.9	808.3

TABLE 5: PROPERTIES OF SELECTED GASES

We will now look at gases used every day for cryogenic purposes and several of their basic characteristics.

1. Liquid Oxygen

- Blue color caused by the presence of the polymer or long-chain molecule O₄.
- Boils at 90.18 K and freezes at 54.4 K.
- Density = 1141 kg/m³
- Oxygen is slightly magnetic (paramagnetic) in contrast to the other cryogenic fluids, which are nonmagnetic.
- Because of its chemical activity, oxygen presents a safety problem in handling.
- Oxygen with an atomic number of 16 has three stable isotopes of mass numbers 16, 17, and 18.

2. Liquid Nitrogen

- Produced commercially by distillation of liquid air.
- Clear, colorless fluid that resembles water in appearance.
- Boils at 77.36 K and freezes at 63.2 K.
- Density is 807kg/m³.
- Nitrogen with an atomic number of 14 has two stable isotopes with mass numbers 14 and 15.

3. Liquid Argon

- Is a clear, colorless fluid

- Is inert and nontoxic
- Boils at 87.3 K and freezes at 83.8 K
- Argon has three stable isotopes of mass numbers 36, 38, and 40.

4. Liquid Neon

- Is a clear, colorless liquid
- Boils at 1 atm at 27.09 K and freezes at 24.54 K
- Neon is inert, has a larger heat of vaporization per unit volume, and has a higher density making it an attractive refrigerant
- Neon (atomic weight = 20.183) has three stable isotopes of mass numbers 20, 21, and 22

5. Liquid Fluorine

- A light yellow liquid
- Having a normal boiling point of 85.24 K (153.4°R)
- Liquid fluorine is one of the most dense cryogenic liquids (density at normal boiling point = 1507 kg/m³)
- Will react with almost all inorganic substances
- Fluorine is highly toxic

6. Liquid Hydrogen

- One of the lightest of all liquids
- Hydrogen is quite flammable
- Hydrogen is Paramagnetic
- Natural hydrogen is a mixture of two isotopes: ordinary hydrogen (atomic mass = 1) and deuterium (atomic mass = 2)

7. Liquid Methane (Principal constituent of natural gas)

- Principal component of natural gas
- Clear, colorless liquid
- Boils at 1 atm at 111.7 K and freezes at 88.7 K

THERMODYNAMIC LAWS, EQUATIONS AND THEORY GOVERN ING OPERATING PARAMETERS FOR CYROGENIC PROCESSES:

Basic refrigeration and cryogenic cycles involve the removal of heat from a substance. Most commercial cryogenic processes involve sub-cooling and pressurizing a gas thereby, producing the liquid phase. This brings us to the definition of heat.

“Heat is defined as the form of energy that is transferred across a boundary by virtue of a temperature difference or temperature gradient”.

Implied in this definition is the very important fact that a body never contains heat, but that heat is identified as heat only as it crosses the boundary. Heat is a transient phenomenon.

We start also by defining the three laws of thermodynamics:

FIRST LAW: During any cycle a closed system undergoes, the cyclic integral of heat is equal to the cyclic integral of work. In an open system, matter crosses the boundary and in doing so carries a certain amount of energy into that system. Thus, the energy of the system is influenced by heat, work and matter crossing the system boundary. If we “refine” this definition, we find: the change in the internal energy of a system is equal to the heat added to the system minus the work done by the system.

SECOND LAW: It is not possible for heat to flow from a colder body to a warmer body without any work having been done to accomplish this flow. Energy will not flow spontaneously from a low temperature object to a higher temperature object. This precludes a perfect refrigerator. The statements about refrigerators apply to air conditioners and heat pumps, which embody the same principles.

THIRD LAW: The third law of thermodynamics states that as the temperature approaches absolute zero (0 K); the entropy of a system approaches a constant (and minimum) value. The entropy of a perfect crystalline state is zero at 0 K. In this way, the third law provides an absolute reference point for the determination of entropy of any substance. The third law also says that it is not possible for any system to reach absolute zero in a finite number of steps. This effectively makes it impossible to ever attain a temperature of exactly 0 K.

As you might imagine, there are various equations that define in mathematical terms these three laws plus other great discoveries relative to gases. These are as follows:

IDEAL GAS:

BOYLE’S LAW:

Boyle's Law states that the product of the pressure and volume for a gas is a constant for a fixed amount of gas at a fixed temperature. Written in mathematical terms, this law is

$$P V = \text{constant} \quad \text{FORMULA 1:}$$

A common use of this law is to predict how a change in pressure will alter the volume of the gas or vice versa. Such a problem can be regarded as a two-state problem: the initial state (represented by subscript i) and the final state (represented by subscript f). If a sample of gas initially at pressure P_i and volume V_i is subjected to a change that does not change the amount of gas or the temperature, the final pressure P_f and volume V_f are related to the initial values by the equation

$$P_i V_i = P_f V_f \quad \text{FORMULA 2:}$$

IDEAL GAS LAW:

The Ideal Gas Law is one of the Equations of State. Although the law describes the behavior of an ideal gas, the equation is applicable to real gases under many conditions, so it is a useful equation to learn to use. The Ideal Gas Law may be expressed as:

$$PV = NkT \quad \text{FORMULA 3:}$$

Where:

P = absolute pressure in atmospheres

V = volume (usually in liters)

n = number of particles of gas

k = Boltzmann's constant ($1.38 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$)

T = temperature in Kelvin

The Ideal Gas Law may be expressed in SI units where pressure is in pascals, volume is in cubic meters, N becomes n and is expressed as moles, and k is replaced by R, the Gas Constant ($8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$):

$$PV = nRT \quad \text{FORMULA 4:}$$

Another expression for the Ideal Gas Law may be seen as follows:

$$Pv = RT \quad \text{FORMULA 5:}$$

Where:

P = pressure in lbs/Ft²

V = specific volume in Ft.³/ lbm

R = constant having a particular value for each substance in Ft-lb/lbm-° R

T = temperature in ° Rankin

Let's look at "R" values for several common gasses.

<u>GAS</u>	<u>R (Ft-lb /lbm-R)</u>
Air	53.34
Argon	38.66
Carbon Dioxide	35.10
Carbon Monoxide	55.16
Helium	386.0
Hydrogen	766.4
Methane (Natural Gas)	96.35
Nitrogen	55.15
Oxygen	48.28
Steam	85.76

CHARLE'S LAW

Charles' Law is a special case of the ideal gas law. This law only applies to ideal gases held at a constant volume allowing only the pressure and temperature to change.

$$V_i/T_i = V_f/T_f \quad \text{FORMULA 6:}$$

where

V_i = initial volume

T_i = initial absolute temperature

V_f = final volume

T_f = final absolute temperature

It is extremely important to remember the temperatures are absolute temperatures measured in Kelvin, **NOT** °C or °F.

$$PV = mRT \quad \text{FORMULA 7:}$$

Where:

V = volume in Ft³

m = mass in lbm

P = pressure in lb/Ft²

R = gas constant

T = temperature in ° R

From the relationship above, it may be seen that:

$$P(1)V(1)/T(1) = P(2)V(2)/T(2) \quad \text{FORMULA 8:}$$

Where (1) is the initial state of the gas and (2) is the final state of the gas.

$$m = \eta M \quad \text{FORMULA 9:}$$

Where:

m = mass in lbm

η = moles

M = molecular weight

From these equations is derived: $PV = \eta MRT$ **FORMULA 10:**

MIXTURE OF GASES

$$m \text{ (total)} = m(a) + m(b) + m(c) + \dots + m(n)$$

$$\eta \text{ (total)} = \eta(a) + \eta(b) + \eta(c) + \dots + \eta(n)$$

$$P \text{ (total)} = p(a) + p(b) + p(c) + \dots + p(n)$$

$$V \text{ (total)} = v(a) + v(b) + v(c) + \dots + v(n)$$

REFRIGERATION CYCLES:

It is important to start this discussion with several definitions relative to the science of thermodynamics. The definitions that follow will, in my opinion, be a great help in understanding the various cooling cycle "schemes" used in commerce and industry today.

- An isobaric process is a thermodynamic process in which the pressure remains

constant: $p = 0$.

- An isochoric process also called an iso-volumetric process, during which volume remains constant.

- *_ An isothermal process is a change in which the temperature remains constant: $\Delta T = 0$.*
- *_ A polytropic process is a thermodynamic process that obeys the relation:*

$$PV^n = C,$$

Where P is pressure, V is volume, n is any real number (the polytropic index),

and C is a constant.

- *Saturation temperature designates the temperature at which vaporization takes place at a given pressure, this pressure being called the saturation pressure.*
- *Adiabatic process—A process in which there is no transfer of heat.*

REFRIGERATION AND CRYOGENIC CYCLES

This course will not provide detailed descriptions on all cycles commercially available—only those most popular and most used in commerce today. In this fashion, we will be able to describe the basics and how processes must work in order to bring about sub-zero cooling. The various cycles available today are as follows:

- Linde
- Claude
- Cascade System
- Kaptiza
- Cascade
- Vuilleumier
- Rankin
- Collins

CARNOT CYCLE

We need to start by describing the “perfect” thermodynamic system—the CARNOT Cycle. The Carnot cycle is the ideal cycle and provides the baseline for evaluating the efficiency and operation of other cycles. As we know, it is impossible to have a heat engine that obtains one hundred percent (100%) efficiency therefore, we ask the question: what cycle will provide the maximum efficiency? The first step in defining the “ideal process” is to define a reversible process. A reversible process for a system is defined as one in which, once having taken place, can be reversed and leaves no change in either the system or its surroundings. The efficiency of all heat engines is less than one hundred percent (100%).

A heat engine generally receives heat from a high-temperature reservoir and rejects heat to a low-temperature reservoir. Since we are dealing with reservoirs, we recognize that both high-temperature and low-temperature are constant and remain constant regardless of the amount of heat transferred. Let's further assume this heat engine which operates between high and low temperatures operates on a cycle in which every process is reversible. If every process is reversible, the cycle is also reversible, and if the cycle is reversed, the heat engine becomes a heat pump. This is called the Carnot cycle and is named after a French engineer, Sadi Carnot, who stated the second law of Thermodynamics. A line diagram of the Carnot cycle may be seen as follows:

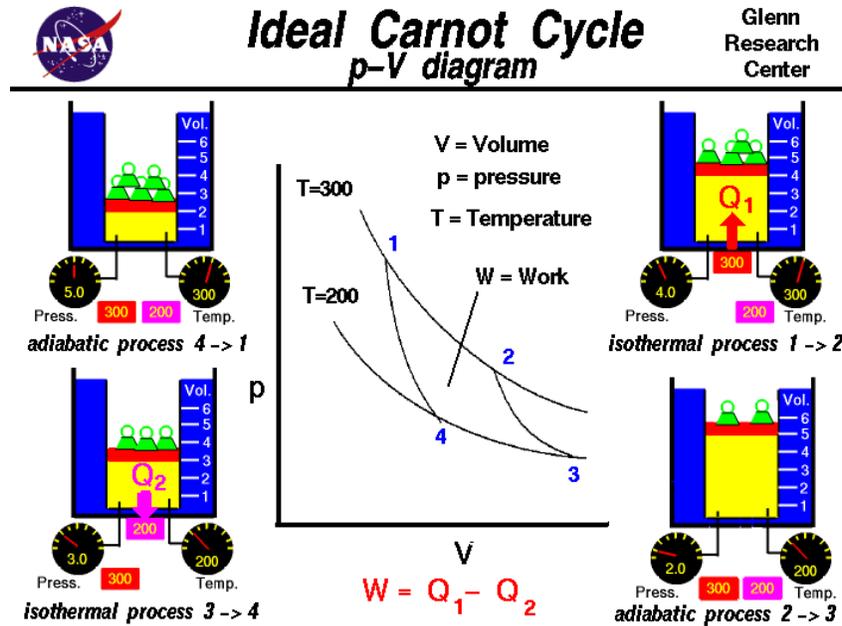


FIGURE 5: IDEAL CARNOT CYCLE

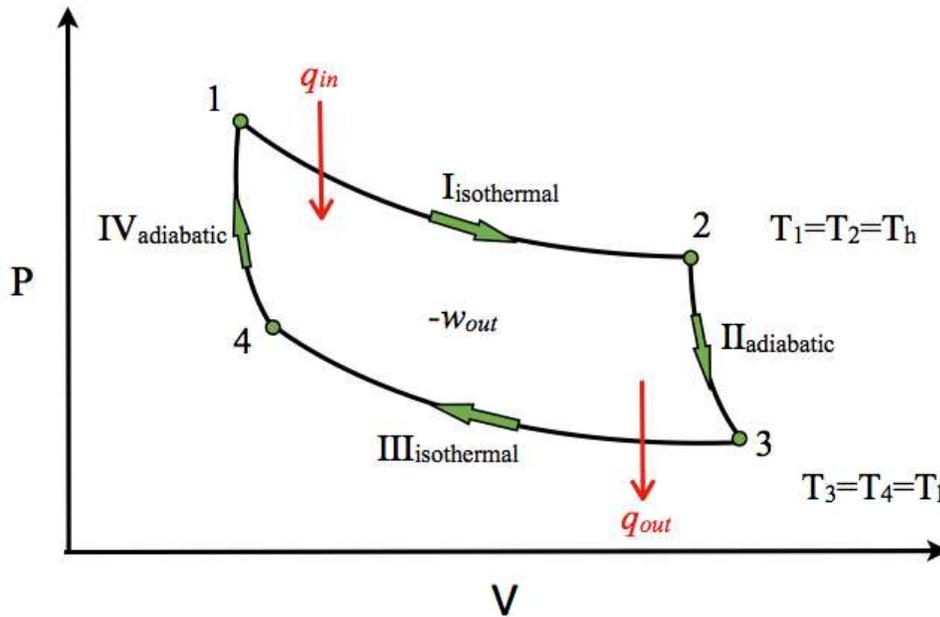


FIGURE 6: pv DIAGRAM FOR CARNOT CYCLE

The first process in the Carnot cycle is a reversible isothermal process in which heat is transferred from the high-temperature reservoir to the working fluid. A change of phase from liquid to vapor at constant pressure is of course an isothermal process for a pure substance. The next process occurs in the turbine. It occurs without heat transfer and is adiabatic. Since all processes in the Carnot cycle are reversible, this must be a reversible adiabatic process, during which the temperature of the working fluid decreases from the temperature of the high-temperature reservoir to the temperature **of the low-temperature** reservoir. In the next process, heat is rejected from the working fluid to the low-temperature reservoir. This must be a reversible isothermal process in which the temperature of the working fluid is infinitesimally higher than that of low-temperature reservoir. In the final process, which completes the process, is a reversible adiabatic process in which the temperature of the working fluid increases from the low temperature to the high- temperature. NOTE: It is impossible to construct an engine which operates between two given reservoirs that is more efficient than a reversible engine operating between the same two reservoirs. This is the reason the Carnot cycle represents our baseline for performance.

LINDE CYCLE:

The most elementary air liquefaction method is the simple Linde cycle. This cycle is given by the following figure:

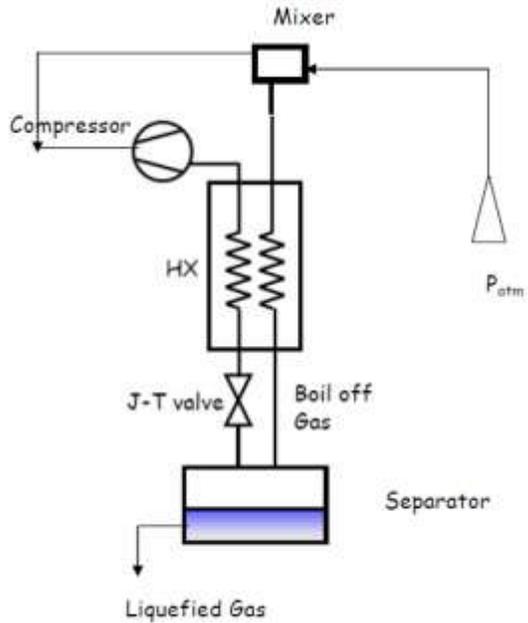


FIGURE 7: REPRESENTATION OF LINDE CYCLE

The equipment includes a compressor, heat exchanger and separator. The heat exchanger and separator must be extremely well insulated. The working diagram for the process is given as:

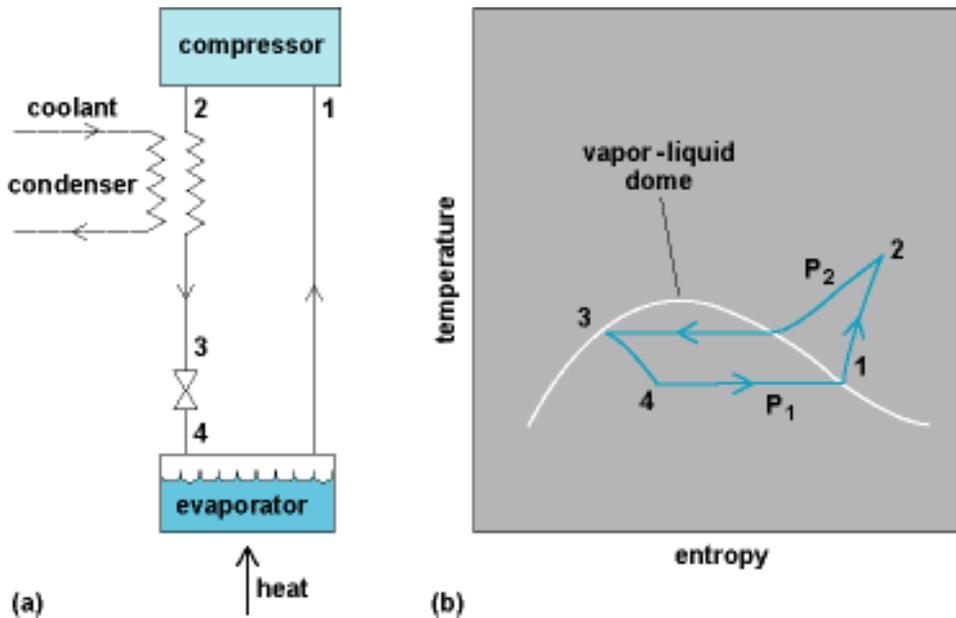


FIGURE 8: pv DIAGRAM OF LINDE CYCLE

In the heat exchanger, high –pressure air is cooled sufficiently so liquid air may result from the throttling process. The system will pull itself down to operating conditions after start-up from a warm condition providing the temperature of the air leaving the compressor is less than the inversion temperature. Two performance quantities are of particular interest in gas liquefaction systems. These are 1.) Yield in pounds of liquid produced per pound of gas compressed and 2.) The specific work consumption in Btu per pound of liquid compressed. The single-stage Linde system is a fairly inefficient method of cooling. For this reason, the dual-pressure Linde cycle was developed and is definitely an improvement relative to efficiency.

CLAUDE SYSTEM:

The elementary Claude air liquefaction system differs from the Linde cycle by the addition of an expansion engine and a second regenerative heat exchanger. This system is shown by the diagram below:

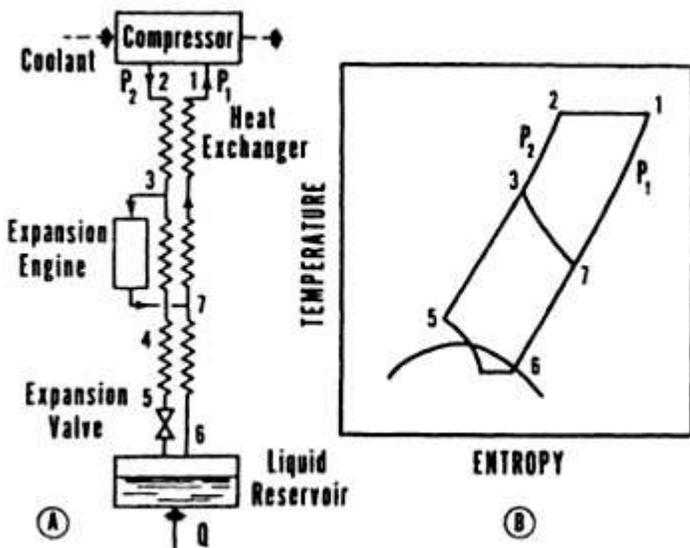


FIGURE 9: pv DIAGRAM OF CLAUDE CYCLE

CASCADE SYSTEM:

Cascade and absorption refrigeration systems are used for industrial refrigeration applications. The cascade refrigeration system is commonly used for industrial application that incorporates two or more refrigeration cycles in series. This is done to acquire low temperatures, which cannot be achieved with a single refrigeration cycle. Refrigerant enters the compressor as a saturated vapor. As the refrigerant is compressed, it increases in temperature and pressure (points 1-2). After the compress or the refrigerant passes through the condenser heat energy (QH) is exchanged in the heat exchanger causing the refrigerant to cool and become a saturated liquid (points 2-3). The heat energy rejected by the first condenser is absorbed by the second systems evaporator located in the heat exchanger (points 2-9).

Next, the refrigerant passes through the second compressor, which increases the temperature of the refrigerant even higher (points 4-9). The refrigerant then passes through the second condenser giving off heat energy (QH) causing the refrigerant to cool (points 4-5). Then the refrigerant is passed through the second throttling valve, which causes the fluid to expand and decrease in temperature (points 5-6). Next, both refrigerants from the first and second stage mix in the flash chamber creating a liquid vapor mixture (points 6-7). The mixture then passes through another throttling valve and reduces the temperature even farther (points 7-6). Finally, the refrigerant passes through the evaporator, and it absorbs heat energy (QL) from the environment that it is trying to cool. The refrigerant exits the evaporator as a saturated vapor and returns to the compressor to begin the process all over again (points 8-1). The cascade refrigeration operates the same as a regular refrigeration unit except for the second stage of operation. The absorption refrigeration cycle is used as a method of absorbing heat energy with fluids as the working medium. Ammonia/water, lithium bromide/water, and ammonia/sodium thiocyanate are primarily used for absorption refrigeration systems. The limitation of this system is operating temperature. Because most commercial and industrial refrigeration **applications** occur at temperatures below 32°F, the required input temperature must be at least 230°F. The source of heat energy required to meet the temperature requirements come from geothermal energy, solar energy, and waste heat from cogeneration plants and process steam plants. The absorption system contains the same components as a vapor compression cycle except that it has an absorption device that consists of a rectifier, absorber, generator, and pump. The general premise of the absorption system is to transfer heat energy from one medium to another. Heat pumps systems, cascade refrigeration systems, and absorption systems all operate on the theory of ideal vapor compression cycle. Although there are many different types of refrigeration systems that exist, they all operate with the same objective: To reduce the temperature of a closed environment.

RANKINE SYSTEM:

The Rankine refrigeration system is a thermodynamic cycle in which heat is converted to work or work to heat. The Rankine cycle is adopted as the theoretical basis for an approximate computation of real cycles in steam power plants. The cycle is named after W. J. Rankine, one of the founders of the science of thermodynamics.

In the Rankine cycle, the working fluid (water) is converted to steam in a boiler and then superheated at constant pressure in a superheater. The steam expands adiabatically in a steam turbine, thus performing work. The steam then is condensed at constant pressure in a condenser, and the condensate is first pumped to an economizer for preheating and then returned to the boiler for conversion into steam.

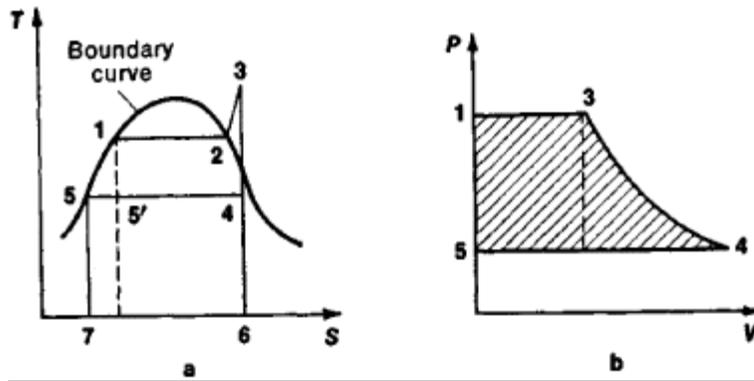


FIGURE 10: pv DIAGRAM OF RANKINE SYSTEM

The figures above show Rankine cycle: (a) curve representing various states of temperature T and entropy S , (b) diagram of the Rankine cycle showing pressure P and volume V ; (1–2) conversion of water into steam upon the application of heat, (2–3) superheating of the steam, (3–4) adiabatic expansion of the steam, (4–5) condensation of the steam, and (5–1) preheating of the water

The work performed by 1 kg of steam in a Rankine cycle is represented by the area 1–2–3–4–5 in the phase diagram. The thermal efficiency of the cycle is equal to the ratio of this work to the total amount of heat supplied to this kg of steam, which is seen in area 1–2–3–4–6–7–5. The efficiency of a Rankine cycle using saturated steam is 0.29–0.36; with superheated steam, it is 0.34–0.46. The Rankine cycle differs from the Carnot cycle in that the heating of the water and the **superheating of** the steam proceed at constant pressure and increasing temperature. It is inadvisable to execute the Carnot cycle with steam because the condensation would have to be effected to point 5' and the steam-water mixture would then have to be compressed along the adiabatic 5'-1. Additional energy would therefore be required.

STEELS REQUIRED WHEN OPERATING WITHIN CRYO-CYCLES:

Designers of cryogenic assemblies base their stress calculations on the room-temperature properties of the material. The reason is that it is the highest temperature the material will encounter. And it stands that if a higher-strength material that stands up to super cold conditions were available, designers might specify it.

At 26°C austenitic stainless steel has tensile and yield strengths that are 172 MPa greater than the corresponding strengths for type 304 stainless. At -100°C it's tensile and yield strength exceed those of type 304 by 550 MPa and 276 MPa respectively.

A grade with the following chemical composition shows good mechanical properties at cryogenic temperatures:

C - 0.072%

Mn - 16%

P - 0.02%

S - 0.008%
Si - 0.41%
Ni - 5.85%
Cr - 17.8%
N - 0.36%
Fe - Remainder

(The composition is given for plates with 12.7mm thickness)

The material combination of high strength, good toughness, and weldability should prompt designers to specify it for welded pressure vessels for the storage of cryogenics.

Steels for Low-Temperature

When designing low-temperature systems or equipment, the engineer finds that notch toughness ranks high in importance because a part or structure will generally fail due to a notch or other stress concentration. Test results measure the steel's capacity to absorb energy, and thus signify its ability to resist failure at points of local stress concentration.

Fatigue limit of steel also must be considered. At low temperatures, systems are usually subjected to dynamic loads, and structural members to cycle stresses. Examples include vessels that frequently undergo pressure changes and large structures and mobile equipment that experience extreme stress imposed by packed snow or high winds. Other considerations include heat conductivity and thermal expansion.

Carbon steels have a better weldability, greater toughness, and higher strength with low coefficients of thermal conductivity than alloy steels. The A 516, one of the most frequently used group of carbon steels, have tensile strengths ranging from 379 MPa to 586 MPa minimum. The big advantage of A 516 steels is their low initial cost.

Compared with A 516, A 442 class has higher carbon and manganese in plates less than 25.4 mm thickness, and lower manganese beyond 25.4 mm. However, applications for A 516 Grades 55 and 60 duplicate those of A 442. They are easier to fabricate than A 442 grades because carbon content is lower.

Higher strength with good notch toughness is available in carbon steels A 537 Grade A and A 537 grade B. They can be normalized or quenched and tempered to raise yield and tensile strength and impact toughness beyond those of the A 516's. Table 1 shows mechanical properties at low temperatures for some typical ASTM carbon steels.

Table 1. Specifications for Low-temperature Steels

Designation	Lowest usual service temperature, (°C)	Min Yield Strength (MPa)	Tensile Strength (MPa)	Min Elongation, L0= 50 mm (%)	Uses
A442 Gr. 55	-45	221	379 - 448	26	Welded pressure vessels and storage tanks; refrigeration; transport equipment
A442 Gr. 60	-45	221	414 - 496	23	
A516 Gr. 55	-45	207	379 - 448	27	
A516 Gr. 60	-45	221	414 - 496	25	
A516 Gr. 65	-45	241	448 - 531	23	
A516 Gr. 70	-45	262	483 - 586	21	
A517 Gr. F	-45	690	792 - 931	16	Highly stressed vessels
A537 Gr. A	-60	345	483 - 620	22	Offshore drilling platforms, storage tanks, earthmoving equipment
A537 Gr. B	-60	414	551 - 690	22	
A203 Gr. A	-60	255	448 - 531	23	Piping for liquid propane, vessels, tanks
A203 Gr. B	-60	276	482 - 586	21	
A203 Gr. D	-101	255	448 - 531	23	Land-based storage for liquid propane, carbon dioxide, acetylene, ethane and ethylene
A203 Gr. E	-101	276	482 - 586	21	
A533 Gr. 1	-73	345	552 - 690	18	Nuclear reactor vessels where low ambient toughness required for hydrostatic testing; some chemical and petroleum equipment
A533 Gr. 2	-73	482	620 - 793	16	
A533 Gr. 3	-73	569	690 - 862	16	
A543 Gr. 1	-107	586	724 - 862	14	Candidate material with high notch toughness for heavy-wall pressure vessels
A543 Gr. 2	-107	690	793 - 931	14	

TABLE 6: STEELS USED FOR CRYOGENIC PURPOSES

Since a variety of low-temperature steels are available, the engineer must consider the advantages each has to offer according to the application. The cost-strength ratio is but one factor; others, such as welding and fabrication costs, have equal or greater bearing on final costs. However, heat-treated carbon grades are often used for low-temperature services. Besides offering excellent low-temperature toughness plus fabricability, these grades are lower in initial cost.

Pipeline Steels for Low-Temperature Uses

Steels for natural gas pipelines must meet more demanding requirements than that used for oil. For example, they carry compressed gas at -25°C to -4°C , making crack growth and brittleness a problem in the severe arctic environment. Achieving low-temperature notch toughness, grain size control, and low sulfur content were among major problems in developing the steel, particularly since economic feasibility had to be considered.

Hot-rolled steels present a good opportunity to cut both cost and weight if the cost per unit strength could be reduced. As strength of high-strength, low-alloy steels rise, toughness usually drops.

In steel alloyed with molybdenum, manganese and columbium, which is use for these pipelines, molybdenum raises both strength and toughness. Carbon is reduced to make columbium more soluble, and to improve weldability and impact strength. Steels with small and large amount of columbium have similar precipitation kinetics; higher strengths are produced by larger quantities of columbium. Columbium also promotes hardenability, which is needed to develop an acicular-ferrite microstructure. Manganese, along with molybdenum, helps to inhibit transformation to polygonal ferrite on the steel.

Where sulphur cannot be kept low, however, rare earth additions will control the shape of the sulfide inclusions. During hot working, grain refinement is enhanced because columbium has a grain-boundary pinning effect. This effect makes it possible to produce a highly sub-structured austenite prior transformation, which helps in assuring transformation to fine grained acicular ferrite.

Contributing to high strength and good impact resistance is the transformation mechanism - austenite changes to fine-grained acicular ferrite, which is further strengthened by the precipitation of columbium carbonitride. Other advantages include good formability and most important, excellent weldability.

Aside from pipeline, this steel can be used in the automotive, railroad, heavy equipment, construction and shipbuilding industries, application areas in which the keynote is low cost per unit strength. Because of their inherently good strength-toughness relationship, the manganese-molybdenum-columbium steels may well satisfy this requirement.

STORAGE OF CRYOGENIC MATERIALS:

How are cryogenic liquids contained?

Cryogenic liquids are shipped and used in thermally insulated containers. These cryogenic liquid containers are specifically designed to withstand rapid temperature changes and extreme differences in temperature.

Liquid Dewar Flasks

Liquid Dewar flasks are non-pressurized, vacuum-jacketed vessels, somewhat like a "Thermos bottle". They should have a loose fitting cap or plug that prevents air and moisture from entering, yet allows excess pressure to vent. Flasks containing helium, hydrogen and other low-boiling liquids have an outer vessel of liquid nitrogen for insulation.

Laboratory Liquid Dewar Flasks

Laboratory liquid Dewars have wide-mouthed openings and do not have lids or covers. These small containers are primarily used in laboratories for temporary storage.

Liquid Cylinders

Liquid cylinders are pressurized containers specifically designed for cryogenic liquids. This type of container has valves for filling and dispensing the cryogenic liquid, and a pressure-control valve with a frangible (bursting) disk as backup protection. There are three major types of liquid cylinders which are designed for dispensing:

- liquid or gas
- only gas
- only liquid

Cryogenic liquids, such as hydrogen, are usually stored in horizontal or vertical cylindrical tanks. Spherical tanks are sometimes used for larger volumes. Tanks are vacuum-insulated and contain redundant pressure-relief devices as a safety precaution to prevent over-pressurization. These safety measures must be taken to insure catastrophic rupture does not occur.

Permanent storage vessels for liquid hydrogen should be designed, constructed, and tested in accordance with the ASME BPVC or API Standard 620 (Design and Construction of Large, Welded, Low-Pressure Storage Tanks). (Please note: Standards are available and must be consulted when dealing with Cryo-materials. THIS IS A MUST.)

Permanent vessels should have substantial noncombustible supports securely anchored to firm noncombustible foundations. Steel supports greater than 18 inches high should be protected with a coating with a two-hour fire resistance rating.

Mobile containers for liquid hydrogen (i.e., tankers) should be designed, constructed, and tested per DOT specifications and regulations. Liquid hydrogen tankers are equipped with automatic shutoff valves. Transporting cryogenic liquids must be accomplished in approved and well-maintained trucks.

Liquid hydrogen vessel designs should include adequate thermal insulation systems to minimize evaporation losses. Pressure relief is required for both the inner vessel and the vacuum jacket.

The large temperature difference between ambient and cryogenic conditions (temperature difference of 300° F or more) results in significant thermal contraction of most materials, which must be accommodated for in designs for cryogenic service.

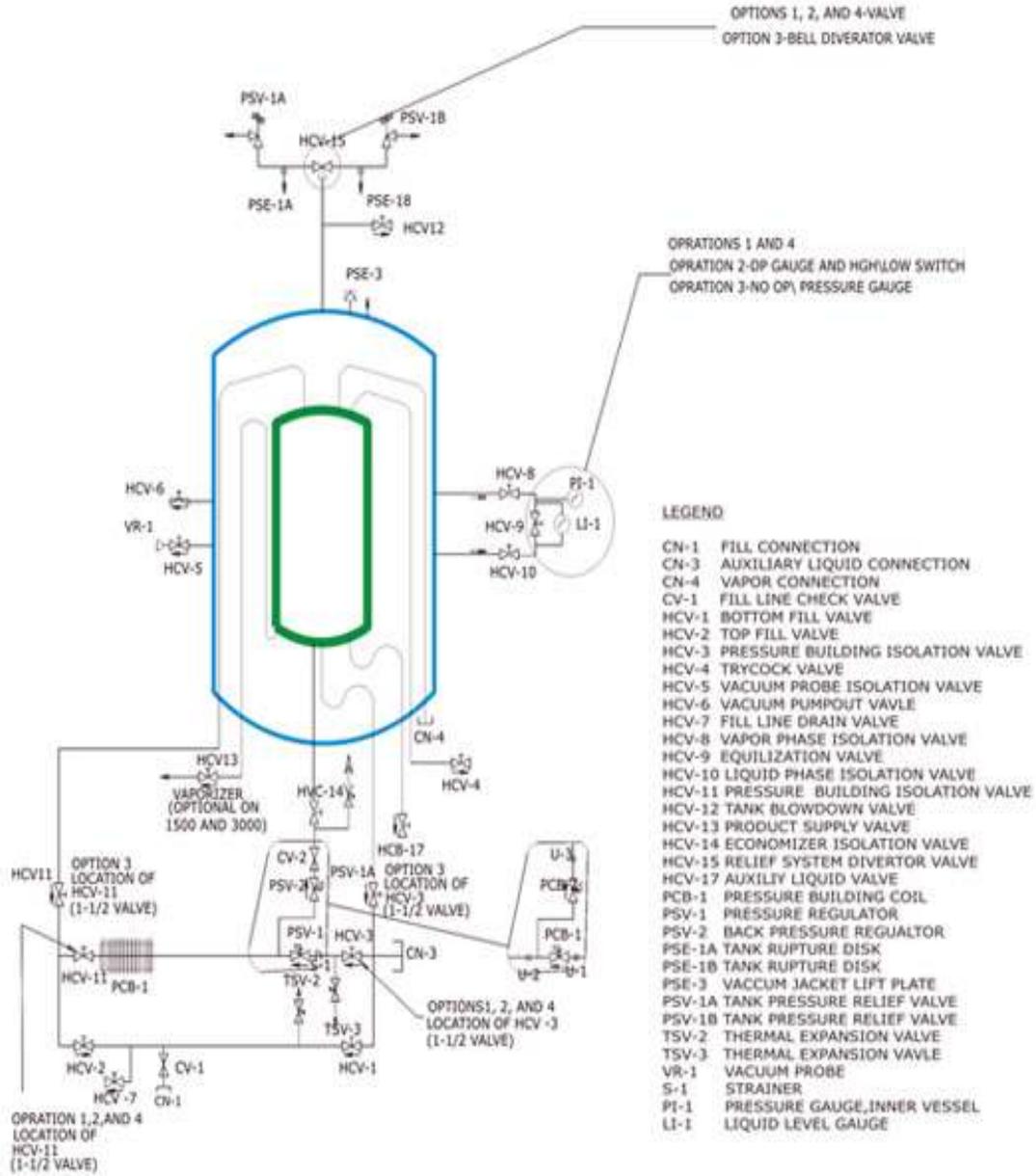


FIGURE 11: REPRESENTATIVE STORAGE CONFIGURATION WITH ASSOCIATED PARTS

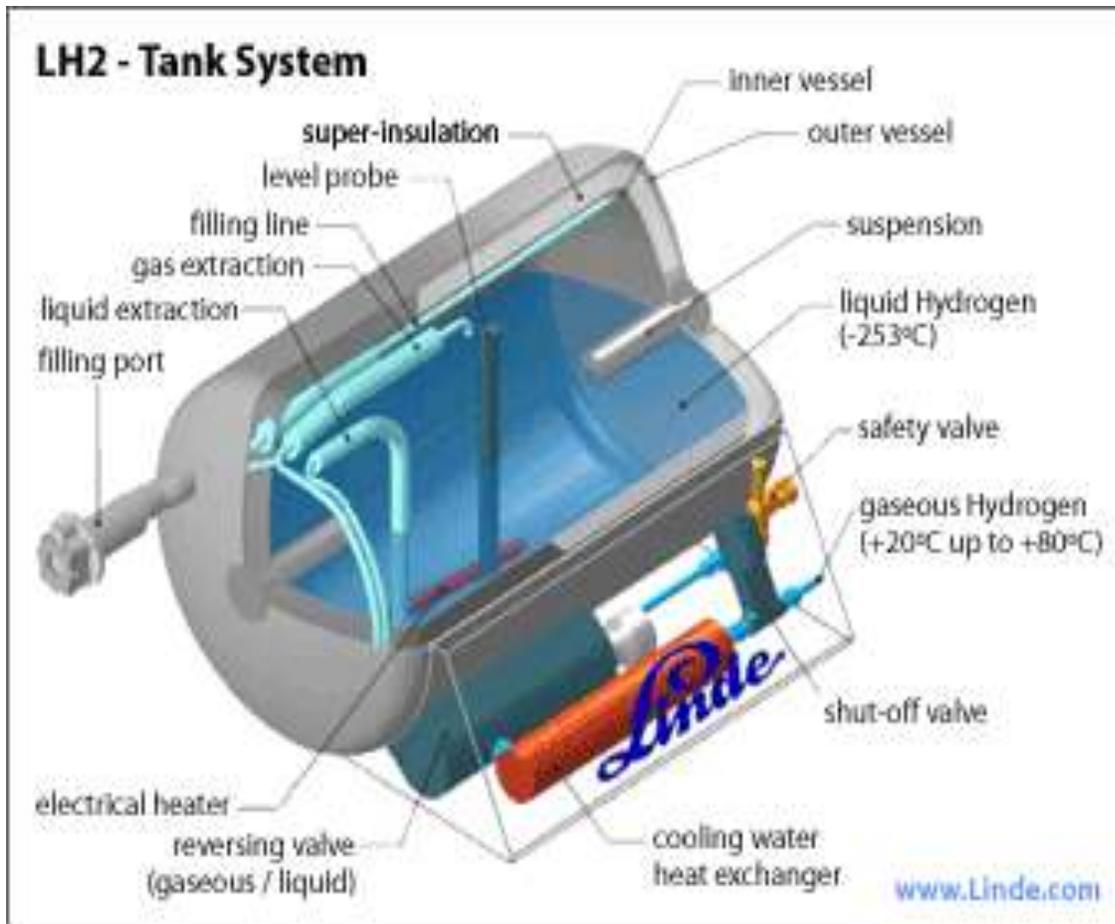


FIGURE 12: REPRESENTATIVE LIQUID HYDROGEN STORAGE TANK AND SYSTEM



FIGURE 13: VERTICLE STORAGE TANK FOR LIQUID NITROGEN



FIGURE 14: REPRESENTATIVE STORAGE TANK**FIGURE 15: HORIZONTAL CRYO STORAGE TANK SYSTEMS****PIPING AND TRANSFER OF CRYOGENIC LIQUIDS:**

As you might suspect, the transfer of liquefied gases is a specialty in itself and significant care must be taken to transport the liquids from point to point. This will definitely involve an inner passageway surrounded by appropriate insulation encapsulated by an outer passageway. The method used to transfer the material is called “cryo-pumping”. Not surprisingly, the development of cryo-pumping went in parallel with the advances made in liquefaction (liquid nitrogen, 77.3 K, Dewar, 1874; liquid hydrogen 20.4 K, Dewar, 1898; liquid helium, 4.2 K, Kammerlingh Onnes, 1908). It was soon found that vacuum can be produced by charcoal kept at these cryogenic temperatures. The successful use of liquid-nitrogen-cooled traps to prevent oil back-streaming from diffusion pumps was reported in the 1910s by Gaede and Langmuir. However, the first large-scale applications of cryo-pumping were triggered by the first space projects in the 1950s. They often included operation with liquid hydrogen. In the second half of the last century, liquid helium bath-cooled cryo-pumps were very popular for laboratory applications, when oil contamination was requested (so that diffusion pumps could not be used) and manual re-fill was not a problem. The next big step forward was the development of cryogen-free regenerative refrigerators by Gifford and McMahon in 1960. These devices have seen a significant progress towards higher cooling power at lower end temperatures, and their development continues.

By international classification, a cryo-pump is defined as a vacuum pump which captures the gas by surfaces cooled to temperatures below 120 K. To achieve vacuum in a closed volume means, simply

speaking, to remove all molecules in the gaseous phase within this volume. According to the different physical principles, which are exploited to create, improve or maintain vacuum, there are different types: – Positive displacement or mechanical pumps, which provide volumes to be filled with the gas being pumped. The volumes are cyclically isolated from the inlet; the gas is then transferred to the outlet. In most types of positive displacement vacuum pumps, the gas is compressed to atmosphere before the discharge at the outlet. Positive displacement pumps work independently of the gas species to be pumped. – Kinetic pumps, which impart momentum to the gas being pumped in such a way that the gas is transferred continuously from the pump inlet to the outlet. – Entrapment or capture vacuum pumps, which retain gas molecules by chemical or physical interaction on their internal surfaces.

Together with the getter and the sputter ion pump, the cryo-pump is the most prominent representative of the latter group. As for all high-vacuum pumps (i.e., pumps working below the 10–3 Pa range) an appropriate medium fore pressure has to be provided by a mechanical fore pump, before the cryopump can be started. The fore pump is also needed to exhaust the gas to the atmosphere. Whereas this gas transfer is done continuously in the case of kinetic and positive displacement pumps, entrapment pumps do this in a batch-wise manner as they accumulate the gas during pumping and must be regenerated from time to time. During actual pumping, the gases within the entrapment pump systems are instantaneously immobilized and no outlet is required at all.



FIGURE 16: INSULATED PIPING FOR TRANSPORTING CRYOGENIC LIQUIDS

TEMPERATURE MEASUREMENT DEVICES FOR CRYO MATERIALS:

Temperature resolution and accuracy are important, but are not the only considerations when choosing a temperature sensor and its associated measurement system. Other considerations include: sensor size or thermal mass, stability over time, response time, mechanical shock resistance, interchangeability, measurement system simplicity, cost, magnetic field effects, and resistance to ionizing radiation. The scope of this paper is limited to the estimation of resolutions and accuracies possible when making

cryogenic temperature measurements with commercially available temperature sensors. Cryogenic temperature sensors have been developed based on a variety of temperature-dependent properties. Common, commercially available sensors include resistors, capacitors, thermocouples, and semiconductor junction devices such as diodes or transistors. The temperature dependent characteristics of such sensors are published elsewhere. Primary standards-grade sensors are very sensitive to thermal and mechanical shock and are therefore not suitable for ordinary laboratory or industrial temperature measurements. Other temperature measurement techniques such as gas, vapor pressure, acoustic, noise, and magnetic susceptibility thermometry, are not covered by this paper as they require much greater effort to implement or they severely constrain system design. Temperature resolution is the smallest temperature change that can be detected. The precision (or reproducibility or stability) is a measure of how closely the measured values are grouped. Accuracy is indicated by the difference between measured and true values of a parameter. The accuracy of a single measurement can be no better than the resolution, but is degraded by calibration and measurement errors. The relevant equations for determining resolution and accuracy depend on whether the measurement is of the absolute temperature or of a temperature change. In either case, the achievable resolution depends on 1) the sensor characteristics and 2) the measurement system resolution. The accuracy of a temperature measurement can be evaluated using error analysis.

SUMMARY:

I hope from this course you can see the remarkable value of cryogenics and how the technology enhances our every-day lives. We certainly live better with the vast applications given us today. I would also hope you will use this course as the “spring board” for additional study and discovers.

CRYOGENICS

APPENDIX

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CRYOGENICS

REFERENCES

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USEFUL RELATIONSHIPS

- 1 PSI = 144 PSF = 2.04 inches Hg = 27.7 inches of water
- 1 inch Hg = 0.49 PSI = 13.6 inches of water
- 1 inch of water = 0.0361 PSI
- 1 standard atmosphere = 14.696 PSI = 29.2 inches of Hg
- 1 Hp = 33,000 Ft-lbs / minute
- 1 Hp = 2 545 Btu/Hr.
- 1 Hp = 746 Watts
- 1 ton of refrigeration removes 200 Btu/min of heat from a substance
- Gravitational constant = 32.174 lbm -Ft/lbf-°R
- Specific gas constant (Air) = R = 53.3 Ft-lbf/lbm-°R
- Density of water = 62.4 lbm/Ft³
- 1 Btu = 778 Ft-lbf
- 1 Hp = 550 Ft-lbf/sec
- 1 Kw = 3412.9 Btu/Hr
- 1 Kw = 1.341 Hp
- 1 ton of refrigeration = 200 Btu/min = 12,000 Btu/Hr

GLOSSARY OF TERMS

Acute Exposure - a short-term exposure usually occurring at high concentration.

Acute Health Effect - an effect that develops either immediately or a short time after exposure.

Auto ignition Temperature - the minimum temperature required to initiate or cause self-sustained combustion, in the absence of a spark or flame.

Bio-hazardous Infectious Material - a material that contains organisms and the toxins produced by these organisms that have been shown to cause disease or are believed to cause disease in either humans or animals.

Boiling Point - the temperature at which a liquid changes from a liquids to a gas, at normal atmospheric pressure.

Carcinogens - agents/compounds that may induce cancer in humans.

CAS Registry Number - a number assigned to a material by the Chemical Abstracts Service (CAS) to provide a single unique identifier.

Chemical Formula - sometimes called the molecular formula, indicates the elements that make up a chemical.

Chemical Name - a proper scientific name for the active ingredient of a product.

Chronic Exposure - a long-term exposure, usually occurring at low concentrations.

Chronic Health Effects - an effect that appears a long time after exposure.

Coefficient of Oil/Water Distribution - the ratio of the solubility of the chemical in oil to its solubility in water.

Combustible Liquid - a liquid which has a flash point above 37.8 C.

Compressed Gas - a material which is a gas at normal room temperature (20 C) and pressure but is packaged as a pressurized gas, dissolved gas or gas liquefied by compression or refrigeration.

Condensation - the process of reducing from one form to another denser form such as steam to water.

Controlled Products - Under the Controlled Products Regulation, a controlled product is defined as a material, product or substance which is imported or sold in Canada and meets the criteria for one or more of the following classes: -

- Class A - Compressed Gas
- Class B - Flammable and Combustible Material
- Class C - Oxidizing Material

- Class D - Poisonous and Infectious Material
- Class E - Corrosive Material
- Class F - Dangerously Reactive Material

Corrosive Material - a material that can attack (*corrode*) metals or cause permanent damage to human tissues such as skin and eyes on contact.

Cryogenics - materials which exist at extremely low temperatures, such as liquid nitrogen.

Dangerously Reactive Materials - materials that may undergo vigorous condensation, decomposition or polymerization. They may react violently under conditions of shock or increase in pressure or temperature. They may also react vigorously with water or water vapour to release a toxic gas.

Decomposition - the breakdown of a substance, often due to heat, decay or other effect, with the release of other compounds such as vapours or gases that may be flammable or toxic.

Density - the weight of a material in a given volume. It is usually given in grams per milliliter (*g/ml*).

Dilution Ventilation - dilution of contaminated air with uncontaminated air in a general area, room or building for the purposes of health hazard or nuisance control, and/or for heating and cooling.

Dose - amount of the agent that has entered the body through the various routes of entry.

Evaporation Rate - the rate at which a liquid changes to vapour at normal room temperature.

Explosive (Flammable) Limits - the lower explosive (*flammable*) limit (*LEL*) is the lowest concentration of vapour in air which will burn or explode upon contact with a source of ignition. The upper explosive (*flammable*) limit (*UEL*) is the highest concentration of vapour in air which will burn or explode upon contact with a source of ignition.

Explosive (Flammable) Range - the range between the lower explosive limit (*LEL*) and the upper explosive limit (*UEL*).

Exposure Limits- established concentrations which, if not exceeded, will not generally cause adverse effects to the worker exposed. Exposure limits differ in name and meaning depending on origin. For example:-

1. The exposure levels for the hazardous chemicals that are included in the Regulation respecting the Control of Exposure to Biological or Chemical Agents - made under the *Occupational Health and Safety Act* of Ontario, are expressed as follow: -

TWAEV Time-Weighted Average Exposure Value: The average airborne concentration of a biological or chemical agent to which a worker may be exposed in a work day or a work week.

STEV Short Term Exposure Value: - The maximum airborne concentration of a chemical or biological agent to which a worker may be exposed in any 15 minute period, provided the TWAEV is not exceeded.

CEV Ceiling Exposure Value: The maximum airborne concentration of a biological or chemical agent to which a worker may be exposed at any time.

SKIN: This notation indicates that direct or airborne contact with the product may result in significant absorption of the product through the skin, mucous membranes or eyes. Inclusion of this notation is intended to suggest that preventative action be taken against absorption of the agent through these routes of entry.

2. Threshold Limit Values (*TLVs*) are exposure guidelines developed by the American Conference of Governmental Industrial Hygienists (ACGIH). They have been adopted by several Canadian governments and others as their legal limits. They are expressed as follows:-

TLV-TWA Threshold Limit Value - Time-Weighted Average: The time-weighted average concentration for a normal 8 hour work day and a 40 hour work week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

TLV-STEL Threshold Limit Value - Short Term Exposure Limit: a 15 minute time-weighted average exposure which should not be exceeded at any time during a work day even if the 8 hr TWA is within the TLV. Exposures at the STEL should not be repeated more than 4 times a day and there should be at least 60 minutes between successive exposures at the STEL.

TLV-C Threshold Limit Value - Ceiling: the concentration that should not be exceeded during any part of the working exposure.

Other exposure limits include the Permissible Exposure Limits (*PEL*) which are legal exposure limits in the United States.

Flammable Limits - "See Explosive Limits".

Flammable Substance - one that will readily catch fire and continue to burn in air if exposed to a source of ignition.

1. **Flammable Aerosol**- a material that is packaged in an aerosol container which can release a flammable material.
2. **Flammable Gas**- a gas which can readily catch fire and continue to burn.
3. **Flammable Liquid** - a material that gives off a vapour which can readily catch fire and continue to burn. A flammable liquid has a flashpoint below 37.8 C.
4. **Flammable Solid**- a material which can readily catch fire and continue to burn vigorously and persistently. This may occur from friction, absorbing moisture, from spontaneous chemical change, or by retaining heat from manufacturing or processing.

5. **Reactive Flammable Material**- a material which is a dangerous fire risk because it can react readily with air or water.

Flashback - this occurs when a trail of flammable material is ignited by a distant source of ignition. The flame then travels back along the trail of gas, vapour or aerosol to its source.

Flashpoint - the lowest temperature of a liquid at which it gives off enough vapour to form an ignitable mixture of vapour and air immediately above the liquid surface.

Freezing Point - the temperature at which a liquid becomes a solid, at normal atmospheric pressure.

Hazard- the potential for harmful effects.

Hazardous Combustion Products - chemicals which may be formed when a material burns. These chemicals may be flammable, toxic or have other hazards.

Hazardous Decomposition Products - formed when a material decomposes (*breaks down*) because it is unstable, or reacts with materials such as water or oxygen in air.

Hazardous Ingredient - Under the Hazardous Products Act, a chemical must be listed in the Hazardous Ingredients section of a MSDS if:-

- it meets the criteria for a controlled product;
- it is on the Ingredient Disclosure List;
- there is no toxicological information available; or
- the supplier has reason to believe it might be hazardous.

Hazardous Polymerization - Polymerization is a process of forming a polymer by combining large numbers of chemical units or monomers into long chains (*polyethylene from ethylene or polystyrene from styrene*). Uncontrolled polymerization can be extremely hazardous. Some polymerization processes can release considerable heat or can be explosive.

Ingestion - means taking a material into the body by mouth (*swallowing*).

Inhalation - means taking a material into the body by breathing it in.

Irritant - some sort of aggravation of whatever tissue the material comes in contact with.

LC50 - the concentration of a material in air which causes death in 50% of a group of test animals. The material is inhaled over a set period of time, usually 4 hrs. LC stands for lethal concentration.

LD50 - the weight of material which causes the death in 50% of a group of test animals. It is usually expressed in weight of material per weight of test animal. LD stands for lethal dose.

LEL (Lower Explosive Limit) - See "Explosive Limits".

Local Exhaust Ventilation - involves the capture of pollutants at the source.

Material Causing Immediate and Serious Toxic Effects - classified under "Poisonous and Infectious Material" as toxic or very toxic based on information such as the LD50 or LC50.

Material Causing Other Toxic Effects - classified under "Poisonous and Infectious Material" as a material causing toxic effects such as skin or respiratory sensitization, carcinogenicity, mutagenicity, etc.

Melting Point - the temperature at which a solid material becomes a liquid.

Mutagen - an agent that affects the genes or cells of the exposed people in such a way that it may cause cancer in the exposed individual or an undesirable mutation to occur in some later generation.

NA Number - See "UN number".

Odor Threshold - the airborne concentration, usually in part per million, at which an odour becomes noticeable.

Oxidizing Material - gives up oxygen easily or can readily oxidize other materials.

Permissible Exposure Limits (PEL) - legal limits in the U.S.A. set by the Occupational Safety and Health Administration (*OSHA*).

pH - a measure of the acidity or basicity (*alkalinity*) of a material when dissolved in water.

Polymer - a natural or man-made material formed by combining units, called monomers, into long chains.

Polymerization - a process of forming a polymer by combining large numbers of chemical units or monomers into long chains.

Parts Per Million (ppm) - represents the concentration of gases or vapour in air. For example, 1 ppm of a gas means that 1 unit of the gas is present for every 1 million units of air.

Sensitization - the development, over time, of an allergic reaction to a chemical.

Solubility - the ability of a material to dissolve in water or another liquid.

Solvent - a material which is capable of dissolving another chemical.

Specific Gravity - the density of a liquid compared to the density of an equal amount of water.

Stability - the ability of a material to remain unchanged in the presence of heat, moisture or air.

Teratogen - agents or compounds that a pregnant woman takes into her body that generate defects in the fetus.

TLV - See "exposure Limits".

Toxicity - ability of a substance to cause harmful effects.

Trade Name - the name under which a product is commercially known.

TWA - See "Exposure Limits".

UEL (Upper Explosive Limits) - See "Explosive Limits".

UN Number - a four digit number assigned to a potentially hazardous material or class of materials. UN (*United Nations*) numbers are internationally recognized and are used by fire fighter and other emergency response personnel for identification of materials during transportation emergencies. NA (*North American*) numbers are assigned by Transport Canada and the US Department of Transport to materials they consider hazardous and to which a UN number has not been assigned.

Vapour - a gaseous form of a material which is normally solid or liquid at room temperature and pressure.

Vapour Density - the density of a vapour compared to the density of an equal amount of air.

Vapour Pressure - the pressure of a vapour in equilibrium with its liquid or solid form.

Ventilation - the movement of air.

Volatility - the ability of a material to evaporate.