CRYOGENICS

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Just as the quest for Atomic Energy enabled us to achieve very high temperatures (of the order of hundreds of thousands of degrees) and gave us what is now called the Plasma State, our exploration of the outer space has brought us in contact with temperatures reaching almost absolute zero (-273 C). The coldest spots on the face of this earth have a temperature around -68°C (in the Arctic Circle).

The term 'Cryogenics' applies to the study of materials at temperatures ranging from -100°C to almost absolute zero (-273°C). This is the range where gases turn into liquids; steel, even rubber, becomes as brittle as glass; metals become super-conducters and even living cells pass into a state of suspended animation.

The cryogenic range may be further subdivided into two parts—cold (up to-200°C) and very cold (below -200°C). The most common atmospheric gases, oxygen, nitrogen and argon, etc., when liquefied, reach temperatures around -200°C whereas hydrogen and helium, reach temperatures below-250°C.

It has been observed that oxygen and nitrogen, when cooled to liquid hydrogen or liquid helium temperatures, acquire the appearance and mechanical properties similar to that of sand.

These days most of these liquids are being manufactured in millions of tonnes per year and used for a variety of purposes. This article discusses some of the applications, such as:

(i) Improved performance of oil wells.
(ii) Manufacture of more compact computer memories.
(iii) Breeding of better cattle by artificial insemination.
(iv) Economic transport of food, etc.
(v) Super-conductivity of metals.
(vi) Study of frozen free radicals.
(vii) Use in Maser, Laser, Infrared Detectors.
(viii) Catalysis at low temperatures.
(ix) Powdering chemical products.

Methods of Producing Low Temperatures

Joule-Thomson Effect: The first landmark in the production of low temperatures was the discovery that sudden expansion of a gas lowers the temperature. This is due to what is known as Joule-Thomson Effect.

This was followed by the realisation that gases could not be liquefied unless they were cooled below the critical temperature.

Making use of these two principles, scientists succeeded in liquefying all the gases which were considered permanent, i.e., unliquefiable at that time.

Claude Expansion Engine: The real breakthrough in the production of low temperatures on a large scale came in 1902, when Claude pioneered the use of the expansion engine. This engine was based on the principle of removing heat as mechanical work.

Kapita's Improvement: Kapita, a Russian physicist and a colleague of Rutherford, the celebrated British nuclear scientist, extended the basic principle used by Claude. He made use of a turbine, instead of an engine.

Properties of Materials at Low Temperatures

A striking demonstration of a tremendous change in the properties of materials, when they are cooled to very low temperatures, can be given by dipping a hollow rubber ball in liquid air and then smashing it to pieces by striking it against a wall or a hard floor.

Man's flight into space where there are temperatures of the order of -200°C or less has initiated a systematic and quantitative study of the various physical and chemical properties of materials.

Tensile Strength of Metals

It has been observed that metals, which have a body-centered-cubic lattice, show a pronounced increase in yield strength and a corresponding loss of ductility with decreasing temperature. The important examples are iron, tungsten and molybdenum. Obviously, these metals are unsuitable for the construction of a low-temperature apparatus. On the other hand, metals which have a face-centered-cubic lattice, show only a slight increase in yield strength and retain their room temperature ductility up to a temperature as low as 77°K. The important examples are copper, nickel and aluminium or their alloys. Consequently, they are used for the construction of low temperature apparatuses.

However, ductility alone is not an adequate guide to the suitability of materials; impact strength must also be considered.

Ours is the age of plastics. Plastics are replacing the conventional materials in almost all branches of human experience. Though Teflon and glass fibre laminates have stood up well in performance tests, more remains to be learnt about the behaviour of plastics.

Thermal Properties

Before discussing thermal properties, it must be remembered that specific heat is not a constant quantity, particularly in the case of metals. It increases with the rise in temperature. For example, a piece of copper requires 6000 times as much heat in raising its temperature from 300° to 301°K as from 2° to 3°K. Some of the metals show thermal conductivity maxima in the range 20° to 50°K. In this range, pure metals have conductivities 100 times as much as their alloys.

The figure given below shows the thermal conductivities of three principal types of solids, namely metals, alloys and dielectrics, particularly sapphire. Sapphires are now made synthetically from aluminium oxide through the technique of growing single crystals. Sapphires are used as gems, as support rods in fire apparatus, as windows and domes for microwave and infra-red systems. They possess high flexural strength at increased temperatures, low loss characteristics and zero porosity.

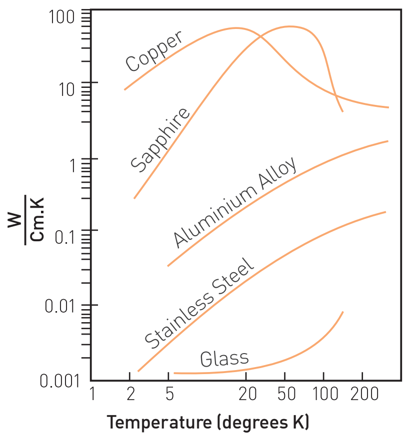

Fig. 1 : Thermal conductivities of some solids of cryogenic temperatures

Properties of Cryogenic Gases

1. Argon: It is present in atmospheric air to the extent of 1 % and can be easily produced in the normal process for the fractionation of air, for oxygen and nitrogen, by putting a few extra plates in the fractionating column. Since it is less expensive than helium, it will gradually replace helium in the shielded arc-welding applications. Of course, we are familiar with its use in electric bulbs and vacuum tubes.

It is also being used for providing an inert atmosphere in those furnaces which heat metals at very high temperatures.

Some Characteristic Properties of Cryogenic Gases

Sl. No.	Gas	Boiling Point	Freezing Point	Range	Production	Main Uses
1.	Argon	-186°C	-189°C	3°C	120 ton/day	(i) Electric bulbs and vacuum tubes (ii) Shielded arc welding torch
2.	Neon	-246°C	-249°C	3°C	—	Electric sign industry
3.	Krypton	-153°C	-157°C	4°C	—	Electronic and lamp industries
4.	Xenon	-163°C	-169°C	6°C	—	Scintillation counters
5.	Hydrogen	-253°C	-259°C	6°C	200 ton/day	(i) Rocket fuel (ii) Thermo-nuclear explosives
6.	Helium	-269°C	Solidifies under high pressure (25 atm)		—	Aeroplane tyres, inert protective atmosphere
7.	Methane	-162°C	-184°C	22°C	—	
8.	Ethylene	-104°C	-169°C	65°C	—	Manufacture of butyl rubber
9.	Nitrogen	-196°C	-210°C	14°C	40-60 billion cubic feet/year	— —
10.	Oxygen	-183°C	-218°C	35°C	150,000 tons/ day,	(i) Welding industries (ii) Steel manufactures (iii) Chemical manufactures

Note: Compare the boiling point-freezing point range of the above cryogenic liquids vis-a-vis normal liquids, e.g. water 100°C, benzene 84°C.

2. Neon: Because of its high density and high heat of evaporation, neon provides three and-a-half times more refrigeration than an equal volume of liquid hydrogen and 40 times more than an equal volume of liquid helium.

3. Krypton: It is 4 times as heavy as neon, 3 times as heavy as nitrogen and 2.6 times as heavy as oxygen. Its high atomic weight reduces evaporation and heat losses from filaments, thus extending their life in addition to enabling them to be operated at higher temperatures.

4. Xenon: The electrical properties of xenon are close to those of mercury and since it does not condense readily, it is used to supplement vapour in some THYRATRON tubes.

5. Helium: Helium is used these days in:

- balloons for weather observation, cosmic-rays studies.
- inert protective atmospheres for welding and metallurgical processing.
- rockets and missiles.
- Aeroplane tyres.

6. Hydrogen: Hydrogen is a favoured propellant because its low density results in higher velocities of the exhaust gases as they emerge from the rocket nozzles and consequently more thrust for a given rate of consumption.

7. Nitrogen: The combination of the low boiling point (-198°C) and the high heat of vaporisation makes liquid nitrogen an economical refrigerant. Nitrogen is used for:

- Bright annealing of stainless steel.
- Flushing, precooling and testing of rockets.
- Supplying an inert atmosphere in the manufacturing of chemicals and metals.
- Artificial insemination.

8. Oxygen: Its use is very widespread. About one-third of total oxygen production is used in steel manufacture, about half in other chemical manufactures and the remaining in the oxyacetylene flames for cutting and welding.

9. Methane: Though not as useful in cryogenics as other cryogenic gases, it is being shipped in large quantities after being liquefied. It is one of the most important and least expensive (since it is available in huge quantities as a constituent of natural gas) raw materials for many industrial materials based on organic compounds.

10. Ethylene: Manufacture of butyl rubber is the only large-scale synthetic organic chemical process which is operated at cryogenic temperatures i.e., -100°C or -148°C. Boiling liquid ethylene is used as the coolant in this process. Perhaps it is the only hydrocarbon gas, which is also used as a low-temperature refrigerant in addition to its being an important starting raw material. Cryogenic techniques are employed in separating it from cracked hydrocarbon gases.

Electrical Properties

It is well known that resistance of metals falls sharply as the temperature is lowered. They can stand a higher current without any damage.

Alloys do not follow this pattern at all. The drop in their resistivity is much lower. For example, constanton – an alloy of 60 parts copper and 40 parts nickel 95% of its resistance retains at cryogenic temperatures (i.e., below -100°C).

Semi-conducting materials such as silicon and germanium offer an interesting combination of properties at low temperatures. They possess a high thermal conductivity and low electrical conductivity.

When we plot electrical resistance as a function of temperature at a certain temperature (different for different metals), there is a sudden drop in electrical resistance and the metal becomes a super-conductor. Many theories have been advanced for this frictionless flow of electricity through solids. A recent theory postulates that electrons move in pairs instead of as individuals and the vibrations of metallic atoms are unable to break the pairs. Obviously, these electrons must be having opposite spins.

This phenomenon is of immense practical value for the operation of high field electromagnets for high energy accelerators.

Measuring Low Temperatures

The ordinary mercury thermometer becomes useless near a temperature of –39°C, its freezing point. Liquid toluene may be used up to –78°C and liquid pentane up to about –180°C. Below this temperature, electrical, magnetic or some other property of substances must be used. The most common property used is the resistivity of some noble metals like platinum or those of the semi-conductors.

Platinum Resistance Thermometer

Variation of the electrical resistance of platinum metal with temperature is quite sensitive and reproducible even up to a temperature of 20° K. The resistance may be measured either by a wheat stone bridge or by a potentiometer. Recently pure Indium has been used up to temperatures as low as 4°K.

Thermistor

One of the advantages with super-conducting materials is that their resistance varies exponentially with temperature. Moreover, they have a negative temperature coefficient; thus lower temperatures give higher resistances and greater sensitivity. In fact, the resistance of a thermistor increases so rapidly as the temperature decreases that it may limit the range of temperatures which can be measured with these devices. Initially carbon was used as the sensing material, but now doped germanium is being used.

Thermocouples

Thermocouples, in which two dissimilar metals fused together generate a voltage at a junction, which is placed at a different temperature than the ends, is a common device for measuring temperatures over a wide range. Though easier to build, they have been found to be less sensitive at lower temperatures. The cold junction used for measurement of low temperatures is liquid nitrogen (-95°C).

Copper-constanton thermocouples have been successfully used up to a temperature of 12°K (-200°C).

Containers for Cryogenic Liquids

Realising that most cryogenic liquids have a low heat of vaporisation, the need to ensure a very effective insulation for any container for them becomes evident.

Liquid	Latent Heat of Vaporization		
Hydrogen	107	cal/gm	
Nitrogen	50	"	
Oxygen	50	"	
Neon	20	"	of water 540 cal/gm
Helium	5	"	

Dewar Vessels: We are all familiar with Thermos flasks which are nothing but double- walled vessels with a high vacuum between the walls and a highly reflecting surface facing the vacuum side. The walls may be made of glass or copper.

Vessels made from Plastic Foams: Blown out plastic materials which contain many small cells, not inter-connected, are good insulating materials. But their efficiency is not as good as that of the evacuated glass or copper vessels, on account of the former's inability to stand repeated thermal expansion and contraction.

Vessels with Annular Space filled with Evacuated Powders: If in addition to evacuating the annular space, it is also filled with fine light powder, such as a silica aerogel, carbon black, perlite, etc., the insulation efficiency is improved further, but it requires the annular space to be at least 10 cm wide. In addition, there are some other operational problems.

Super-Insulation: For handling liquid hydrogen or liquid helium, a considerably improved insulation is required. One way is to make the light aerosol powder opaque to infra-red radiation by mixing it with finely divided copper or aluminium; the other way is to provide radiation-reflecting shields separated from the vessel surfaces and from one another by low conductivity filters. Alternate layers of aluminium foil and glass filter-mats in sandwich fashion, having as many as 80 layers per inch, are being used in commercial storage and transport containers. The space filled with these should be evacuated to 10^{-4} cm Hg.

Application of Low Temperatures

A. Space Research: Space research is a major consumer of the cryogenic fluids using oxygen as a chemical reactant; hydrogen both as a chemical fuel and also as a working medium for nuclear rockets; nitrogen for precooling, flushing and cold flow-testing of rockets; and helium for cryopumping of space simulator chambers (Fig. 2).

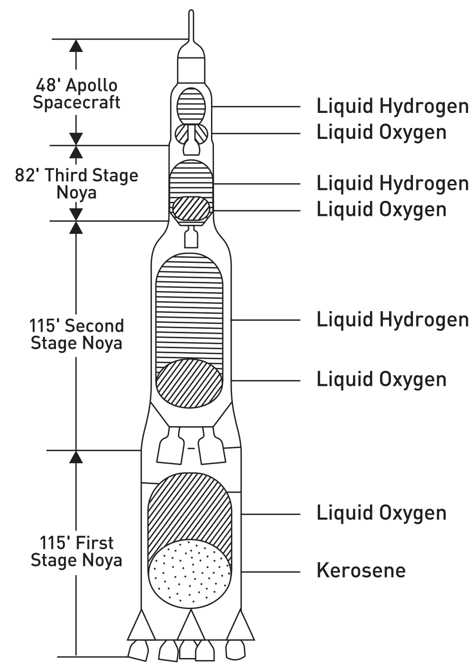

Fig. 2: Section of the Noya-Apollo Spacecraft

B. Biology: Though still quite a few lives are lost due to exposure to cold, particularly by sub-zero temperatures, yet low temperature production has proved a preserver rather than a destroyer of life. It is impossible to think of maintaining Blood Banks without using some cryogenic fluid to preserve the blood.

Bull semen is preserved for subsequent use in artificial insemination. Human organs are preserved at liquid nitrogen temperatures for subsequent use as spare parts in surgery.

Astronauts may be kept in suspended animation for decades in rockets to explore the universe beyond the solar system. Their biological clock could be started at will after their arrival on the desired planet.

Plants, spores and even animals from other planets could be brought safely to the earth for subsequent investigations.

Study of the relation between life and temperature has brought to light certain interesting facts. For example, it has been observed that man can tolerate only a very small increase above normal temperature before he finally succumbs, whereas he can experience a far greater decrease below normal temperature and still survive.

One may also distinguish between the effects produced by cold. Some effects may be due to mechanical injury caused by crystal formation, while others may be due to chemical injury as a result of the increased concentration of salts and other dissolved substances in the remaining fluid. Some of these undesirable effects may be minimised by the use of additives and by controlling the rate of cooling. For example, blood can be frozen uniformly even at the rate of 35°C per minute, whereas sperms, etc., must be preserved by a slow rate of cooling of the order of 5°C per minute.

Fishes save themselves from cold by producing each autumn certain substances which reduce the freezing points of their blood and tissue fluids. Surprisingly cold has little effect on micro-organisms. Certain species have actually multiplied when held at a temperature of –9°C. Live bacteria were found in the human excrement of Captain Scot left in the Antarctic ice about seven decades after his expedition to the Antarctic.

C. Cryo-surgery: Anaesthesia can also be produced by lowering the temperature of the body. In fact, it has many advantages over the anaesthesia produced by the use of chemicals.

Lowering the body temperature retards the entire metabolic process. The patient's oxygen requirements are cut by 50%, circulation slows down and bleeding becomes much more controlled which makes the surgeon's task much easier. If the inner body temperature is maintained around 20°C, the circulation of the blood by the heart can be stopped for about 10 minutes without causing any damage to the brain and other vital organs of the body.

The most difficult part of the human body to be operated upon is the brain. Cryogenics has made bloodless brain surgery possible.

D. Cryotronics or Cryogenic Electronics: Electrical noise in a circuit can be decreased by a factor of 100, by operating the circuit at very low temperatures. There are certain electrical phenomena which occur only at low temperatures. For example:

(a) Operation of Masers

Masers are devices which utilise transitions between energy states of a molecule or atom for amplification of microwave energy. These molecules may be in any state of aggregation, but the most commonly used form is a crystal. When the Maser crystal is operated at low temperatures, the thermal vibrations of the atoms do not interfere with the absorption emission of microwave energy. At low temperatures, the difference in population of atoms between the energy levels, which is the basis of maser action, is greater. In fact, masers work best at liquid helium temperature, but can operate with moderate efficiency at liquid nitrogen temperatures (Fig. 3).

Masers form the heart of radio telescopes which receive signals from objects many millions of light years more distant in space than those visible in the best optical telescopes. Radio astronomy demands very low noise levels in amplifiers because the signals are so weak. In fact, maser radar devices may allow a few ground stations to control the air space of the whole country.

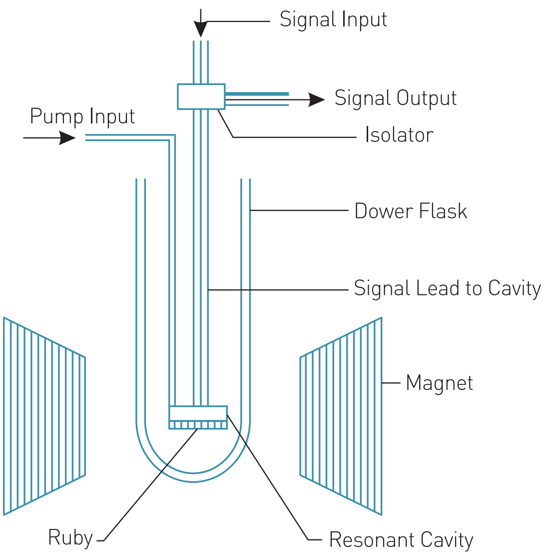

Fig. 3: Typical Maser

(b) Operation of Lasers

Though stimulated emission in the optical region is not as easy as in microwave region, yet when such an emission is produced, the beam is very intense.

Ruby crystals can be used both in masers as well as lasers. The fundamental difference is that in a laser we use the directly excited energy levels of the chromium, while the maser operates on magnetically split levels. Samarium or Uranium ions in a calcium fluoride matrix may prove to be better laser materials than ruby crystals.

Optical frequencies have a number of advantages over radio frequencies for use in communication systems. With more band-width available, more information can be carried. Moreover, since beams are narrow, even smaller antennas can serve the purpose.

Lasers are being used:

(i) As light sources for battle-field illumination.
(ii) As heat sources for welding and cutting of metals.
(iii) In noise-free and interception-proof telephone systems.
(iv) In missile tracking and subsequent destruction.
(v) In communication systems for space.
(vi) In medical sciences for detecting and treating diseases.

E. Infra-red Detectors: Infra-red detectors show improved efficiency and extension of their range to longer wavelengths when they are operated at low temperatures. Moreover, they are simpler, smaller and cheaper than radar equipment. The only disadvantage is that they are subject to interference by fog, etc.

F. Super-Conductivity: Super-conductivity is one of the most intriguing phenomena. It occurs at temperatures very near to absolute zero; the actual temperature varies for different metals and alloys.

There are many theories for the occurrence of this phenomenon, but that of Bardeen and Frohlich, which attributes it to interaction between the conduction electrons and the lattice vibrations of the solid, is the most accepted one.

The first commercial application of super-conductivity was made during World War II. It was for the construction of bolometer, a sensitive thermometric instrument used to detect infra-red rays coming from the equipment of enemy troops.

Super-conductors are of two types: (a) Soft, and (b) Hard.

Aluminium, tin, mercury and lead belong to the first category while inter-metallic compounds like Niobium-tin, Vanadium and Gallium belong to the second.

The soft materials carry the super-conductive current only in a thin surface layer and this super-conductivity is easily destroyed by magnetic fields. The hard materials appear to carry the super-conductive current in thin filaments throughout their structure and are relatively resistant to the effects of magnetic fields. Whereas an ordinary magnet of field strength 50,000 gauss would require an iron core weighing several tonnes and a power supply of 50 kilowatt, a super-conducting magnet of equivalent strength would weigh 200 1bs. (90 kg) including refrigeration and could be operated by a 6-volt storage battery.

Not only super-conducting magnets, but we can also make super-conducting transformers, super-conducting motors and super-conducting switches. Tiny super-conducting switches offer the interesting possibility of scaling down the size of a digital computer without reducing its capacity or speed. In addition to high switching speeds, the cold computers could have a very large memory. In fact, computers which can search 300,000 bits of information in their cryogenic memory and pick out the needed data in 50 micro-seconds are now available.

G. Metal Processing

(i) Steel: Tougher, more ductile steels with improved life characteristics are produced by sub-zero chilling of steel. Those who are familiar with the phase diagrams for steel know that above 204°C steel has a completely austenite structure. As steel cools, the relatively unstable austenite changes slowly to martensite, which is tougher and more ductile. It is most suitable for fabricating dimensionally accurate parts. For example, hacksaw blades, high speed drills, etc.

It is claimed that cold treatment after welding produces a much better finished part because it restores the improvement in strength given by prior cold treatment, which is lost during welding.

(ii) Aluminium: Aluminium alloys which form an important constituent of aircraft manufacture give trouble during machining. Such alloys can be normalised or stress-relieved by subjecting them to low temperatures for an hour or so at temperatures below –100°C. This treatment delays natural hardening.

(iii) Super-alloys: Super-alloys which are finding an increasing use in aircraft and missile industries generate too much heat at the point of contact between the tool and the alloy during machining, with the result that local oxidation of the interface occurs and precise machining becomes impossible. If the solvent which is used to flood the interface is pre-cooled to dry ice temperature (–78°C) and an inert atmosphere from liquid nitrogen provided, tool life can be improved almost 300% in addition to achieving precise machining.

(iv) Miscellaneous Applications

(a) Pulverisation or powdering: To achieve a greater size control, rapid powdering and safety in handling, it is advantageous to pulverise materials like spices, dye-stuffs, pharmaceuticals, insecticides, thermoplastic materials in the frozen state by making them pass in a chamber cooled with liquid nitrogen on their way from the hopper to the pulveriser.

(b) Fire-fighting: Extinguishing fires in the forest is a tedious and laborious job. Use of plastic containers filled with liquid nitrogen as aerial bombs has proved very effective not only in putting out the fire but also in extinguishing cinders. This is probably because of the combination of two effects—cooling and providing an inert atmosphere.

(c) Repairing pipelines without shutting off the main supply: The whole process of cutting and threading the line for installing a local meter does not take more than a few minutes. This can be done by freezing the line with liquid nitrogen.