Module 4 - Cryogenics

Joule-Thomson Effect

Statement: Joule-Thomson effect is the change in temperature that accompanies expansion of a gas without production of work or transfer of heat.

Explanation: If a gas initially at constant high pressure is allowed to suffer throttle expansion through the porous plug of silk, wool or cotton wool having a number of fine pores, to a region of constant low pressure adiabatically, a

change in temperature of gas (either cooling or heating) is observed. This effect is called as Joule–Thomson or Joule-Kelvin effect.

Theory: Consider a gas which expands through fine pores. Let the initial state and final states of the gas be

(P_1, V_1, T_1) and (P_2, V_2, T_2). The Change in temperature $T_1 - T_2 = \partial T$ is due to Joule-Thomson Effect. The external work done by the gas is given by

$$W_1 = P_2V_2 - P_1V_1 \qquad \textbf{(1)}$$

The internal work done by the gas to overcome the intermolecular gases is given by

$$W_2 = -\frac{a}{V_2} + \frac{a}{V_1} \qquad \textbf{(2)}$$

The total work done is by the gas is given by

$$W = W_1 + W_2 = P_2V_2 - P_1V_1 - \frac{a}{V_2} + \frac{a}{V_1} \qquad \textbf{(3)}$$

Van der Waals state equation for the gas is given by

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad \textbf{(4)}$$

Neglecting ab/V^2 the equation (4) could be reduced to

$$PV = RT + Pb - \frac{a}{V} \quad \textbf{(5)}$$

Thus for the initial and final states of the gas we can write

$$P_1V_1 = RT_1 + P_1b - \frac{a}{V_1} \quad \textbf{(6)}$$

$$P_2V_2 = RT_2 + P_2b - \frac{a}{V_2} \quad \textbf{(7)}$$

Substituting equations (6) and (7) in equation (3) and on simplification we get

$$W = R(T_2 - T_1) - b(P_1 - P_2) + \frac{2a}{V_1} - \frac{2a}{V_2} \quad \textbf{(8)}$$

for very small values of a and b in Van der Walls equation it reduces to $PV = RT$ and thus $V = RT/P$. Thus substituting for V_1 and V_2 in equation (8) we get

$$W = R(T_2 - T_1) - b(P_1 - P_2) + \frac{2aP_1}{RT} - \frac{2aP_2}{RT}$$

$$W = R(T_2 - T_1) - b(P_1 - P_2) + \frac{2a}{RT}(P_1 - P_2)$$

Since $\partial T = T_1 - T_2$ and re-organizing the terms, we get

$$W = -R\partial T - b(P_1 - P_2) + \frac{2a}{RT}(P_1 - P_2) \quad \textbf{(9)}$$

$$W = -R\partial T + (P_1 - P_2)\left(\frac{2a}{RT} - b\right) \quad \textbf{(10)}$$

$$W = (P_1 - P_2)\left(\frac{2a}{RT} - b\right) - R\partial T$$

Since the gas is thermally insulated the expansion leads to reduction in temperature ∂T and the Heat lost by the gas is given by

$$W = C_v \partial T \qquad \textbf{(11)}$$

Thus, the equation (10) becomes

$$C_v \partial T = (P_1 - P_2)\left(\frac{2a}{RT} - b\right) - R\partial T$$

$$(C_v + R)\partial T = (P_1 - P_2)\left(\frac{2a}{RT} - b\right)$$

The change in pressure $P_1 - P_2 = \partial P$ and $C_p - C_v = R$ the above equation could be written as

$$\partial T = \partial P \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)$$

Thus, The Joule-Thomson Co-efficient is given by μ_{JT}

$$\mu_{JT} = \frac{\partial T}{\partial P} = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right) \qquad \textbf{(12)}$$

The equation (12) gives the change in temperature of Van der Walls gas when subjected to throttling process.

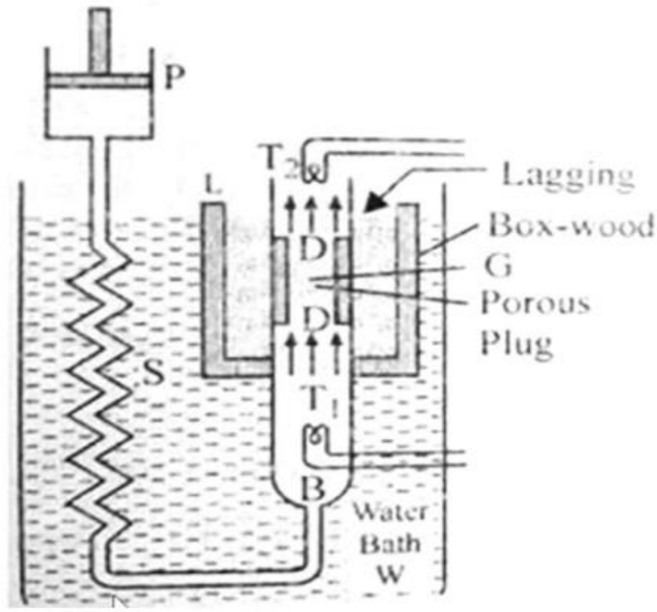
The Three Cases:

1. if $\frac{2a}{RT} > b$ then ∂T is positive and there will be cooling effect.
2. if $\frac{2a}{RT} < b$ then ∂T is negative and there will be heating effect.
3. if $\frac{2a}{RT} = b$ then $\partial T = 0$ indicating neither cooling and nor heating.

<u>Porous Plug Experiment Construction:</u>

Joule in collaboration with Thomson [Lord Kelvin] devised a very sensitive technique known as Porous Plug experiment. The experiment set up of porous plug experiment to study the Joule-

Thomson effect is shown in fig. It consists of the following main parts.



Construction:

1. A Porous plug has two perforated - brass discs $D\&D$ and the space
   between is filled with cotton wool or silk fibres.
2. The porous plug G is fitted in a cylindrical box-wood which is surrounded by a vessel L containing cottonwool to avoid heat exchange with surrounding.
3. $T_1\&T_2$ are two sensitive platinum resistance thermometers used to
   measure the temperatures of the incoming and outgoing gas.
4. The gas is compressed to a high pressure with the help of piston P
   and it is passed through a spiral tube immersed in water bath maintained at a constant temperature.

Experimental Procedure:

1. The experimental gas is compressed by Pump P and is passed slowly and uniformly through the porous plug keeping the high-pressure constant which read by a pressure gauge.
2. During the passage of the gas through the porous plug it is throttled.
3. The gas emerging from the pores of the porous plug expands to atmospheric pressure.
4. Since the expansion of the gas occurs under thermal isolation it is adiabatic.
5. The initial and final temperatures are noted by platinum resistance thermometers $T1\&T2$.

Experimental Results:

Behavior of large number of gases was studied at various inlet temperatures of the gas and the results are as follows:

- At sufficiently low temperatures, all gases show a cooling effect.
- At ordinary temperatures, all gases except Hydrogen and Helium show cooling effect. The Hydrogen and Helium show heating effect.
- The fall in temperature is directly proportional to the difference in pressure on the two sides of porous plug.

Principles of Liquefaction of Gases:

Principle 1 :

When a gas is compressed by a sufficient amount of pressure below its critical temperature results in the reduction of temperature.

Principle 2: If a gas is allowed to evaporate under reduced pressure results in the reduction of temperature.

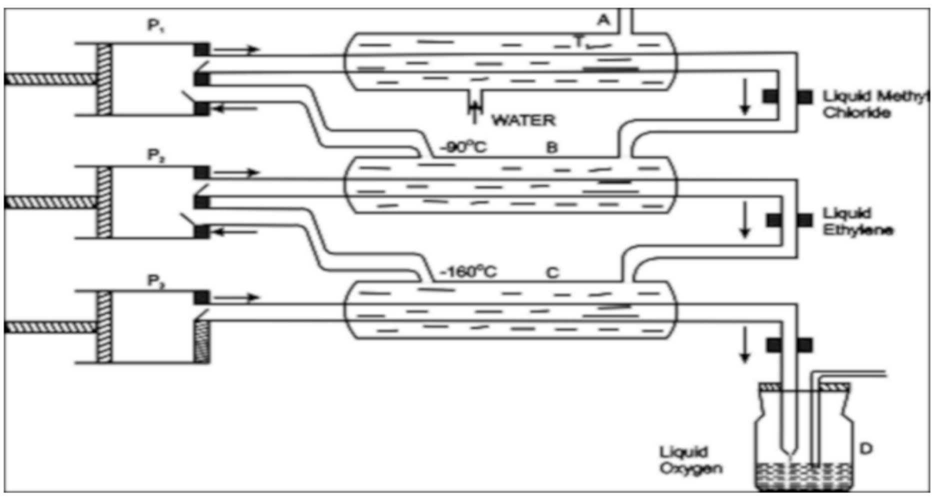
Principle 3: On the basis of the Joule Thomson effect (Porous plug experiment).

Liquefaction of Oxygen by Cascade Process - Pictet Process:

Principle: When a liquid is allowed to evaporate under reduced pressure, it produces high cooling.

Cascade system or Process: When a single stage is not enough to produce the desired result, therefore the process takes place in a number of stages in a sequence:

Construction: The apparatus modified by H K Onnes consists of compression pumps $P1$, $P2$ and $P3$. $T1$, $T2$ and $T3$ are the three tubes which are surrounded by outer jackets A, B and C. 'D' is a Dewar's flask which collects liquid Oxygen



Working:

1. The methyl chloride gas of critical temperature 145°C is compressed by the pump $P1$ through the tube $T1$. It is cooled by the cold water circulating in the jacket A.

2. Here the methyl chloride reaches the temperature lower than its critical temperature. Then it is liquefied under high pressure. The liquid methyl chloride is collected in the jacket B and evaporates under reduced pressure lowering the temperature to -90°C.

3. The ethylene gas of critical temperature 10°C is compressed by the
pump $P2$ through the tube $T2$. It is cooled to -90°C by liquid methyl chloride.

4. Then it is liquefied under high pressure. The liquid ethylene is collected in the jacket C and evaporates under reduced pressure lowering the temperature to -160°C.

5. The oxygen gas of critical temperature - 119°C is compressed to 50
atmospheric pressure by the pump $P3$ and passed through the tube
$T3$.

It is cooled to - 160°C by liquid ethylene in R. Then it is liquefied and the liquid oxygen is collected in the Dewar flask.

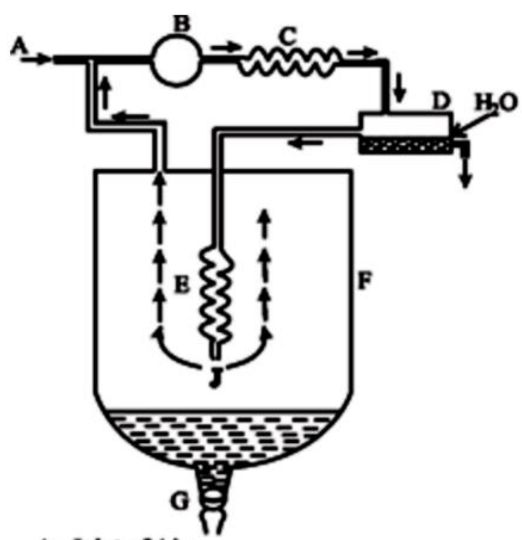
Linde's Air Liquefier Principle:

Linde's process is known as Adiabatic expansion of compressed gas. The process is based upon the combined effect of Joule – Thomson Effect and regenerative cooling.

The compressed gas is made to expand adiabatically and repeatedly.

Linde's Air Liquefaction Construction:

The apparatus used is shown in figure and the parts are labelled.



A - Inlet of Air
B - Compressor
C - Condensing Coils
D - Receiver for Water
E - Copper Spiral with a Jet J
F - Outer Chamber
G - Outlet for Liquefied Air

Process:

- The air is first compressed to about 200 atmospheres in the compressor and then passed through the condensing coils.
- As a result, the air is cooled and the water vapors present condense to form the water which is removed from receiver.
- The dry air is then passed through the spiral copper tube which terminates into a jet.
- The air expands through the jet into the chamber where pressure is about 50 atmospheres.
- Thus, as a result of Joule-Thomson effect, the air is cooled. • As this cooled air moves up, it further cools the incoming air.
- The cooled air is sent to the compressor again and the process is repeated a number of times till ultimately the air is cooled to such an extent that it liquefies.
- The liquefied air gets collected at the bottom of the outer chamber and can be drawn off. Any uncondensed air is recirculated.

Platinum Resistance Thermometer - PRT

Introduction The Platinum Resistance Thermometer uses platinum for determining the temperature.

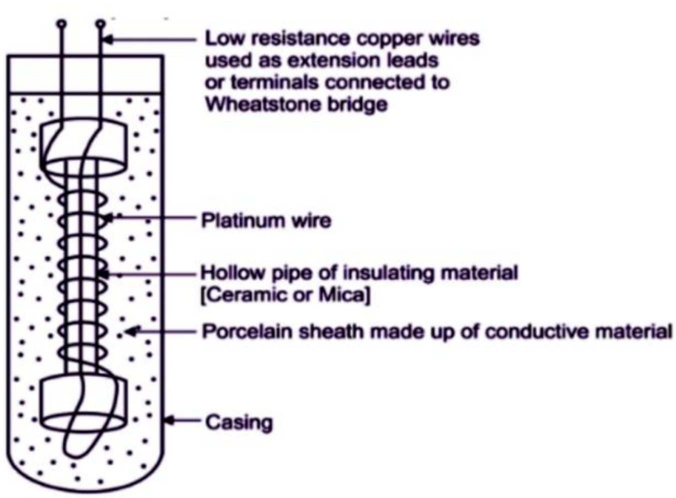
It works on the principle of positive temperature coefficient of resistance. Hence, the resistance of platinum increases with increase in temperature. The platinum is a chemically inert metal and can easily be drawn into fine wires. Because of these properties of platinum, it is used as a sensing element in thermometer.

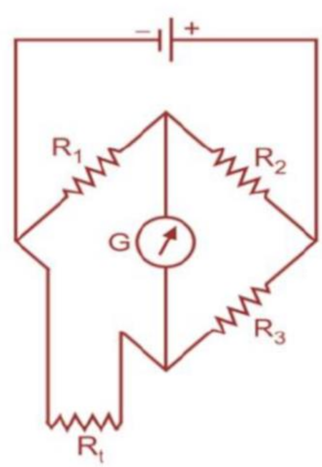
Construction:

- The PRT consists of pure platinum wire wound on hollow pipe made up of insulating mica or ceramic, which is placed in porcelain sheath.
- Free ends of platinum wire are attached to long leads of low resistance copper wires (Fig).
- To measure change in resistance, Wheatstone bridge is used. Two long extension leads form one arm of Wheatstone bridge connect to the copper leads of encapsulated platinum wire.

Working:

- When RTD is subjected to temperature variation the Wheat stone bridge gets unbalanced due to change in resistance Rt of RTD arm.
- This makes the pointer to move over circular scale of galvanometer, which is directly calibrated to give measured value of temperature.





Advantages:

• Linear relationship of resistance with temperature
• The meter gives the precise reading of temperature.
• The thermometer has a wide range from -200°C to 1200°C.
• The thermometer is quite sensitive and possess high accuracy (0.01 °C).
• Platinum possesses stable value of resistance at the given temperature.
• Platinum is chemically inert.

Disadvantages:

• The thermometer gives the slow response.
• The melting point of the thermometer is 1800°C.
• But if platinum measures the temperature higher than

1200°C it starts evaporating.

Applications of Cryogenics

Food Processing:

• Cryogenic quick freezer is widely used in the food cold chain resulting from the better quality of frozen food.
• Due to the rapid freezing rate, water in food will become total or partial vitrification with cryogenic technology.
• Liquid nitrogen (LN2) is used in the freezing process of food.
• Cryogenics is also used transportation of large masses of frozen food.
• Cryogenic food freezing is also helpful for large scale food processing industries.

Aerospace

• For critical components in the aerospace industry the cryogenic

Hardening can be used to strengthen metal parts in communications systems, guidance systems, landing gear, and more.

- Using cryogenic hardening to prep critical components may help the rover survives these bitter cold conditions of lunar night.
- Cryogenics is used to design the multi-layer insulation blankets to insulate the spacecraft.
- Cryogenic engine makes use of Liquid Oxygen (LOX) and Liquid Hydrogen (LH2) as propellants which liquefy at -183 deg C and –253 deg C respectively.

Tribology - Cryogenic Treatment of Metals

- Cryogenic processing (Cryogenic Treatment) typically entails a slow Cooling to cryogenic temperatures, a dwell period at this low temperature followed by a slow return to room temperature and finally, a first stage tempering.
- The cryogenic hardening for steel induces a phase Transformation From austenite to martensite, among other changes. This improves qualities such as hardness, electrical conductivity, wear resistance, lowering friction and susceptibility to corrosion.
- Cryogenic treatment works in creases life of the tools like in Reamers, Tool bits, Tool punches, Carbide Drills, Carbide Cutters, Milling Cutters, Files, Knives, Reciprocating Blades, Dies and cutting tools.
- Stress relieved ferrous and nonferrous castings and forgings for Enhanced dimensional stability and surface finish.

The following are the types of cryogenic treatment

Shallow Treatment: The objects are cooled down to temperature of approximately -85 °C.

Flooding: First the object is taken to -85°C, then the chamber is flooded with
liquid nitrogen to reduce the temperature further.

Deep Cryogenic Treatment (DCT): Subjects the objects to the temperature of approximately -185 °C

<u>Liquefaction of Helium and its Properties</u>

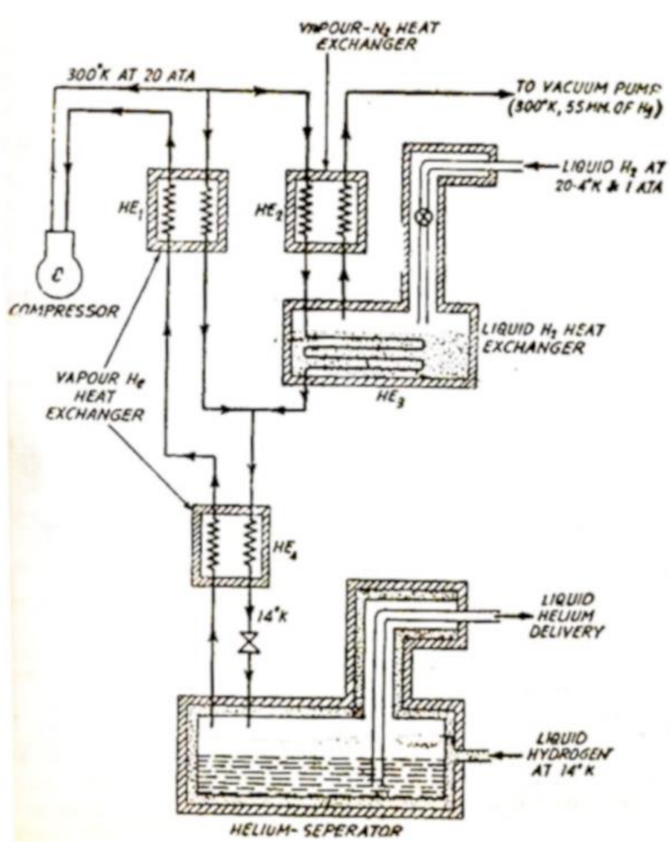
Liquefaction of Helium Introduction:

Helium is the only substance which remains as fluid at temperatures below -269 °C (4K) and its inversion point is much lower than that of Hydrogen namely around -233 °C(40K).

The boiling point of Helium is just around -268.9 °C which is quite close to absolute zero on the Kelvin scale

Principle: Claude's method works on two principles. i.e: Joule Thomson effect and mechanical expansion.

Figure 4.13: Liquefaction of Helium



Working:

- Initially Helium is compressed to a pressure of 20 atmospheres which raises its temperature to the region of 300 degrees Kelvin.
- This compressed high temperature Helium is then split into two streams along different paths.
- The first part of the stream is cooled in the heat exchanger labelled $HE1$ with the help of Helium vapors
- The second part of the stream passes through the heat exchanger $HE2$ to be cooled with Nitrogen vapors cooled by liquid Hydrogen.
- The second part is then passed through liquid Hydrogen heat exchanger $HE3$ • Further the first and second streams are combined and then passed through $HE4$ and again cooled by Helium vapors.
- Finally, the throttle valve is used to initiate the Joule Thomson effect and Helium is collected in the liquid state in the Helium separator.

Properties and Uses

Properties:

- There are two main isotopes of Helium used for liquification namely Helium- 4 and Helium-3.
- There is a slight difference between the properties of the two in terms of their boiling point and critical temperature.
- The boiling point of Helium-3 is even one degree lower than Helium-4. • Liquid Helium exhibits super-fluidity.

Uses:

- Lord Kamerlingh Onnes used liquid helium to study superconductivity of mercury.
- Liquid Helium is used extensively for use in superconducting magnets which need to be cooled to extremely low temperatures. The Superconducting Magnets are in turn used in Magnetic Resonance Imaging and Nuclear Magnetic Resonance.