22PHYM12/22: MODULE 4- Cryogenics

LOW TEMPERATURES IN SCIENCE AND TECHNOLOGY

Cryogenics is defined as that branch of physics which deals with the production of very low temperatures and their effect on matter, a formulation which addresses both aspects of attaining low temperatures which do not naturally occur on Earth, and of using them for the study of nature or the human industry. In a more operational way, it is also defined as the science and technology of temperatures below 120 K. The limit temperature of 120 K comprehensively includes the normal boiling points of the main atmospheric gases, as well as of methane which constitutes the principal component of natural gas. Today, liquid natural gas (LNG) represents one of the largest – and fast-growing – industrial domains of application of cryogenics, together with the liquefaction and separation of air gases.

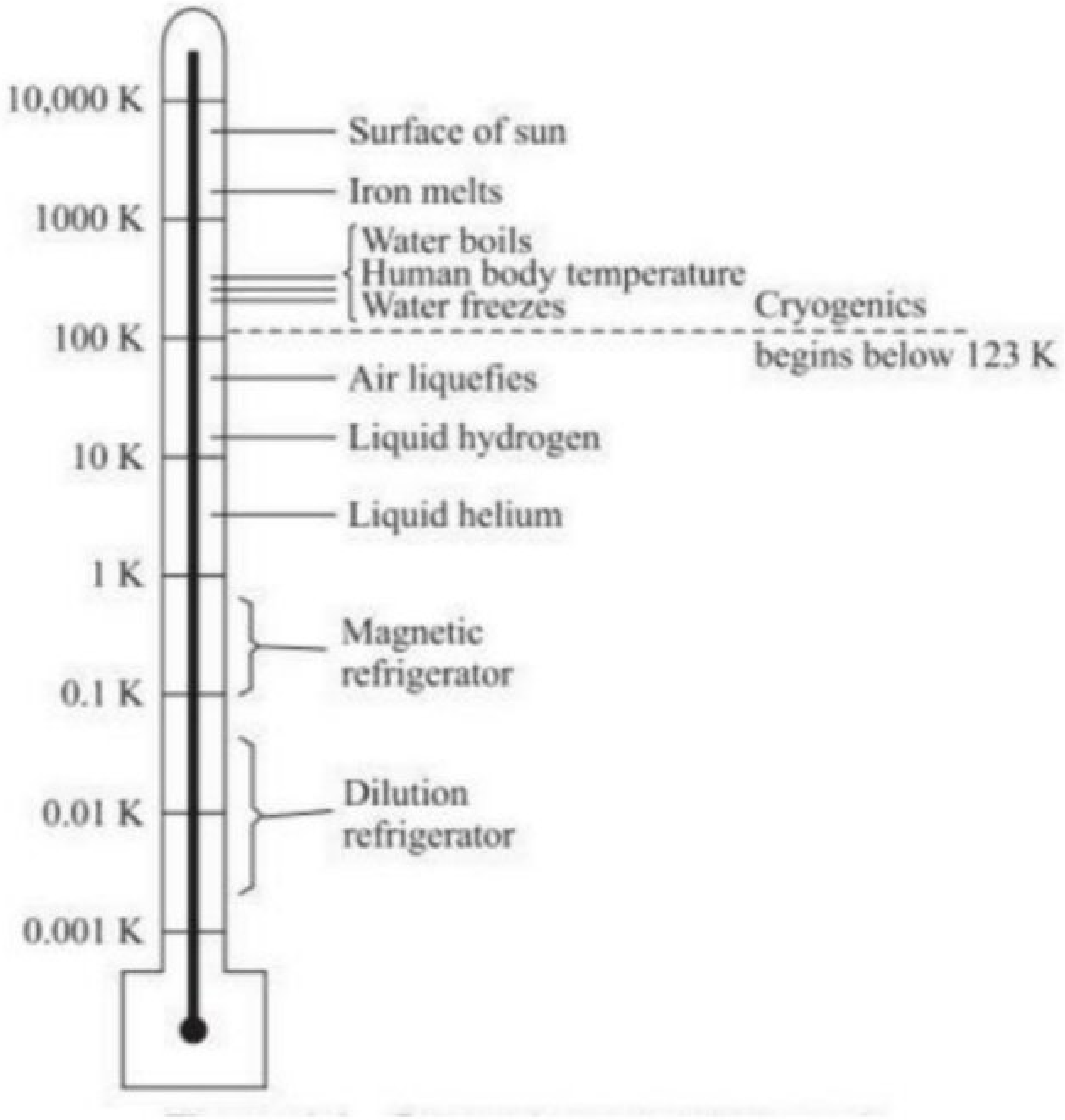


Fig: Cryogenic temperature scale

Joule – Thomson's effect

Statement: 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 of Joule Thomson effect:

Suppose that one mole of gas is allowed to expand through a porous plug from a pressure P_1 and volume V_1 to a pressure P_2 and volume V_2. Let the temperature change from $T_1$to

T_2 due to Joule-Thomson effect.
Net external work done by the gas = $P_2V_2 - P_1V_1$,--------------------- (1)

Now, an internal work is also done by the gas in overcoming the forces of molecular attraction. For a van der Waals gas, the attractive forces between the molecules are equivalent to an internal

Pressure= $\frac{a}{V^2}$, a is a constant

Internal work done by the gas when the gas expands from a volume V_1 to V_2 is $= \frac{a}{V^2}$

Internal work done by the gas when the gas expands from a volume V_1 to V_2 is

$$\int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{a}{V^2} dV = \left[-\frac{a}{V}\right]_{V_1}^{V_2} = \frac{a}{V_1} - \frac{a}{V_2} \; \dots \dots \dots (2)$$

Total work done by the gas = external work +internal work

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

Now, van der Waals equation of state for a gas is

$(P + \frac{a}{V^2})(V - b) = RT$

or $PV = RT + Pb - \frac{a}{V}$ (neglecting $\frac{ab}{V^2}$)

$$P_1V_1 = RT_1 + bP_1 - \frac{a}{V_1} \quad \text{and} \quad P_2V_2 = RT_2 + bP_2 - \frac{a}{V_2}$$

Substituting these values for P_1V_1 and P_2V_2 -in eqn (3) we get,

$$w = R(T_2 - T_1) - b(P_1 - P_2) + \frac{2a}{V_1} - \frac{2a}{V_2} \dots \dots (4)$$

Since a and b are very small, PV=RT or V=RT/P.

Hence, $V_1 = RT_1/P_1$ and $V_2 = RT_2/P_2$.

As T_1 and T_2 are nearly equal, we may write $T_1=T_2=T$ and hence $V_1 = \frac{RT}{P_1}$ and $V_2 = \frac{RT}{P_2}$

Substituting in eq(4) we have, $w = R(T_2 - T_1) - b(P_1 - P_2) + \frac{2a}{RT}[P_1 - P_2]$

Let $T_1 - T_2 = \partial T$. Then

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

$W = (P_1 - P_2)(\frac{2a}{RT} - b) - R\,\partial T$. _-------(5)

Since the gas is thermally insulated, the energy necessary for doing this work is drawn from the K.E. of the molecules. Hence, the K.E. decreases resulting in a fall of temperature by ∂T.
Heat lost by the gas = $C_v\,\partial T$

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

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

$$\text{i.e,} \qquad \partial TC_p = (P_1 - P_2)\left(\frac{2a}{RT} - b\right)$$

$$\delta T = \frac{(P_1 - P_2)}{C_p}\left(\frac{2a}{RT} - b\right) \qquad \ldots\ldots(6)$$

$$\text{Joule THomsan coeffecient,} \qquad \mu_{JT} = \frac{\delta T}{\delta P} = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)$$

Eqn (6) gives the fall in temperature or the cooling produced in a van der Waals gas whensubjected to throttling process.

i) If $\frac{2a}{RT} > b$ then δT is positive. Hence there will be a cooling effect.

ii) If $\frac{2a}{RT} < b$ then δT is negative. Hence there will be a heating effect.

iii) If $\frac{2a}{RT} = b$ then δT =0. Hence there will be neither a heating nor a cooling effect.

Note: For a gas temperature that is above the inversion temperature, the μ_{JT} would be negative. The ∂P shall be always negative in this case, which means that the ∂P must be positive. Consequently, the warming of the gas will take place.

Inversion Temperature:

The temperature at which the Joule –Thomson effect changes sign is called the temperature of Inversion. (T_i). At this temperature $\frac{2a}{RT_i} = b$ or $T_i = \frac{2a}{Rb}$. Thus, above the temperature of inversion, Joule- Thomson effect will be a heating effect and below it a cooling effect.

Porous Plug experiment

Construction:

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.2.1. It consists of the following main parts:

(a) A Porous plug having two perforated -brass discs D & D_1.

(b) The space between D & D_1 is placed with cotton wool or silk fibers.

(c) The porous plug is fitted in a cylindrical box-wood W which is surrounded by a vessel containing cotton wool. This is to avoid loss or gain of heat from the surroundings.

(d) T_1 &T_2 are two sensitive platinum resistance thermometers and they measure the temperatures of the incoming and outgoing gas.

(e) The gas is compressed to a high pressure with the help of piston P and it is placed through a spiral tube immersed in water bath maintained at a constant temperature. If there is any heating of the gas due to compression, this heat is absorbed by the circulating water in the water bath.

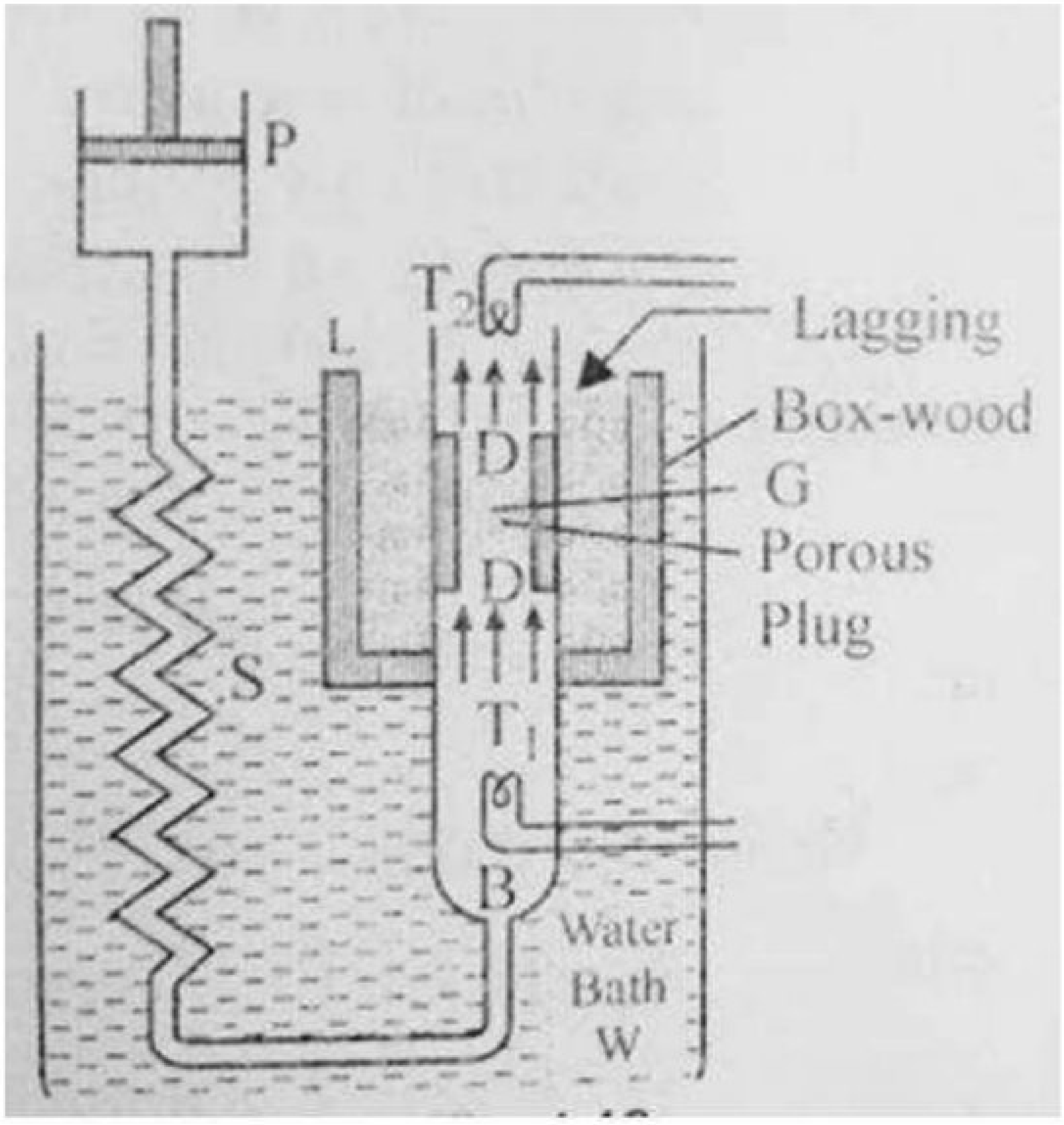


Fig.2.1

Experimental Procedure

The experimental gas is compressed by Pump P and is passed slowly and uniformly through the porous plug keeping the high pressure constant read by pressure gauge. During the passage through the porous plug, the gas is throttled. The separation between the molecules increases. By passing through the porous plug, the volume of the gas increases against the atmospheric pressure. As there is no loss or gain of heat during the whole process, the expansion of the gas takes place adiabatically. The initial and final temperatures are noted by platinum resistance thermometers T_1 & T_2.

Experimental Results

A simple arrangement of porous plug experiment is shown in Fig.2.2 .The behavior of large number of gases was studied at various inlet temperatures of the gas and the results are as follows:

(1)At sufficiently low temperatures, all gases show a cooling effect.

(2)At ordinary temperatures, all gases except hydrogen and helium show cooling effect. Hydrogen and Helium show heating effect.

(3)The fall in temperature is directly proportional to the difference in pressure on the two sides of porous plug.

(4)The fall in temperature for a given difference with rise in the initial temperature of the gas. It was found that the cooling effect decreased with the increase of initial temperature and becomes zero at a certain temperature and at a temperature higher than the temperature instead of cooling heating was observed. This particular temperature at which the Joule – Thomson effect changes sign is called temperature of inversion.

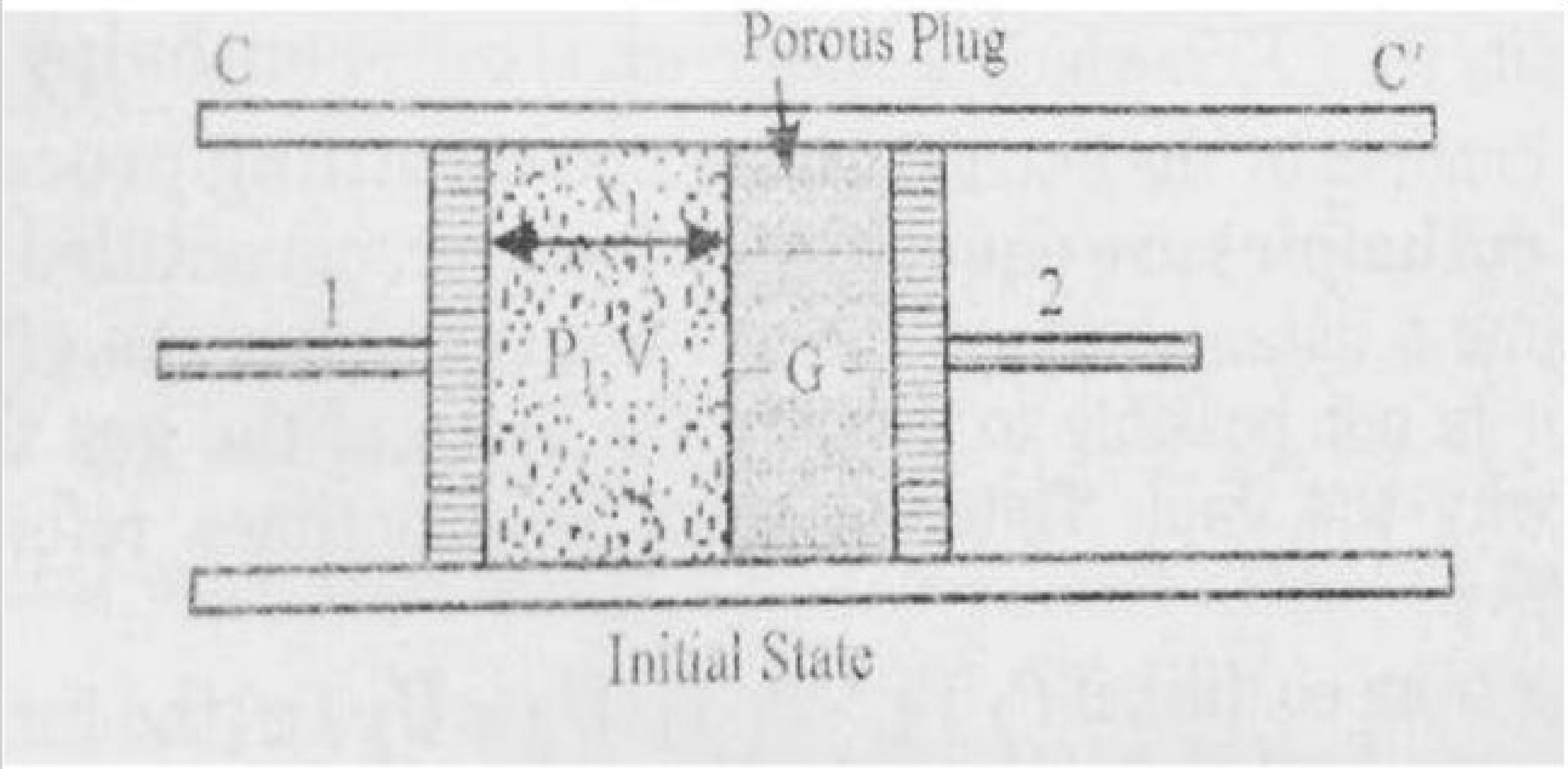


Fig.2.2

Thermo dynamical analysis of Joule Thomson effect:

The arrangement of the porous plug experiment is shown in Fig. The gas passes through the porous plug from the high pressure side to the low pressure side. Consider one mole of the gas. Let P_1, V_1 and P_2, V_2 represent the pressure and volume of the two sides of the porous plug. Let dx be the distance through which each piston moves to the right.

The work done on the gas by the piston 1 = $P_1A_1dx = P_1V_1$
The work done by the gas on the piston 2 = $P_2A_2dx = P_2V_2$
Net external work done by the gas = $P_2V_2 - P_1V_1$

Let w be the work done by the gas in separating the molecules against their inter-molecular attraction.

Total amount of work done by the gas = $(P_2V_2 - P_1V_1) + w$

There are three cases depending upon the initial temperature of gas.

(i) Below the Boyle temperature: $P_2V_2 < P_1V_1$. Then $P_2V_2 - P_1V_1$ is +ve. Hence **w** must be positive. Thus, a net +ve work is done by the gas. Hence, there must be a cooling effect.
(ii) At the Boyle temperature: $P_2V_2 = P_1V_1$, Then $P_2V_2 - P_1V_1 = 0$. The total work done by the gas in this case is w. Therefore, cooling effect at this temperature is only due to the work done by the gas in overcoming inter-molecular attraction.
(iii) Above the Boyle temperature: $P_2V_2 > P_1V_1$. Then $P_2V_2 - P_1V_1$ is –ve. Hence w must be negative. Thus, a net -ve work is done by the gas. Hence, there must be a heating effect.

Thus, the observed effect will depend upon whether $(P_2V_2 - P_1V_1)$ is greater than or less than w.

If $w > (P_2V_2 - P_1V_{1,})$, cooling will be observed.

If $w < (P_2V_2 - P_1V_{1,})$, heating will be observed.

Thus, the cooling or heating of a gas depends on

(i) The deviation from Boyle's law

(ii) Work done in overcoming inter-molecular attraction.

Note: Boyle temperature can be defined as **the point in the temperature range in which a real gas starts to behave like an ideal gas at a pressure range**.

Liquefaction of gases

Definition: **Liquefaction of gases means the process into which the gas substances are converted from gases to a liquid state.**

Principles of Liquefaction of gases

Principle1: In which when a gas is compressed by a sufficient amount of pressure below its critical temperature, as a result liquefaction starts.

Principle2: When we reduce the pressure, and the gas or the liquid is allowed to evaporate, then due to evaporations, it causes cooling.

Principle3: On the basis of the **Joule Thomson effect** (Porous plug experiment).

Liquefaction of Oxygen gas by cascade process (Pictet process):

This process was first used by **Pictet** in 1878. He successfully obtained a small quantity of Liquid Oxygen with the help of pressure applied, and with other liquefied gases.

Cascade system or Process: A process is called the Cascade 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.

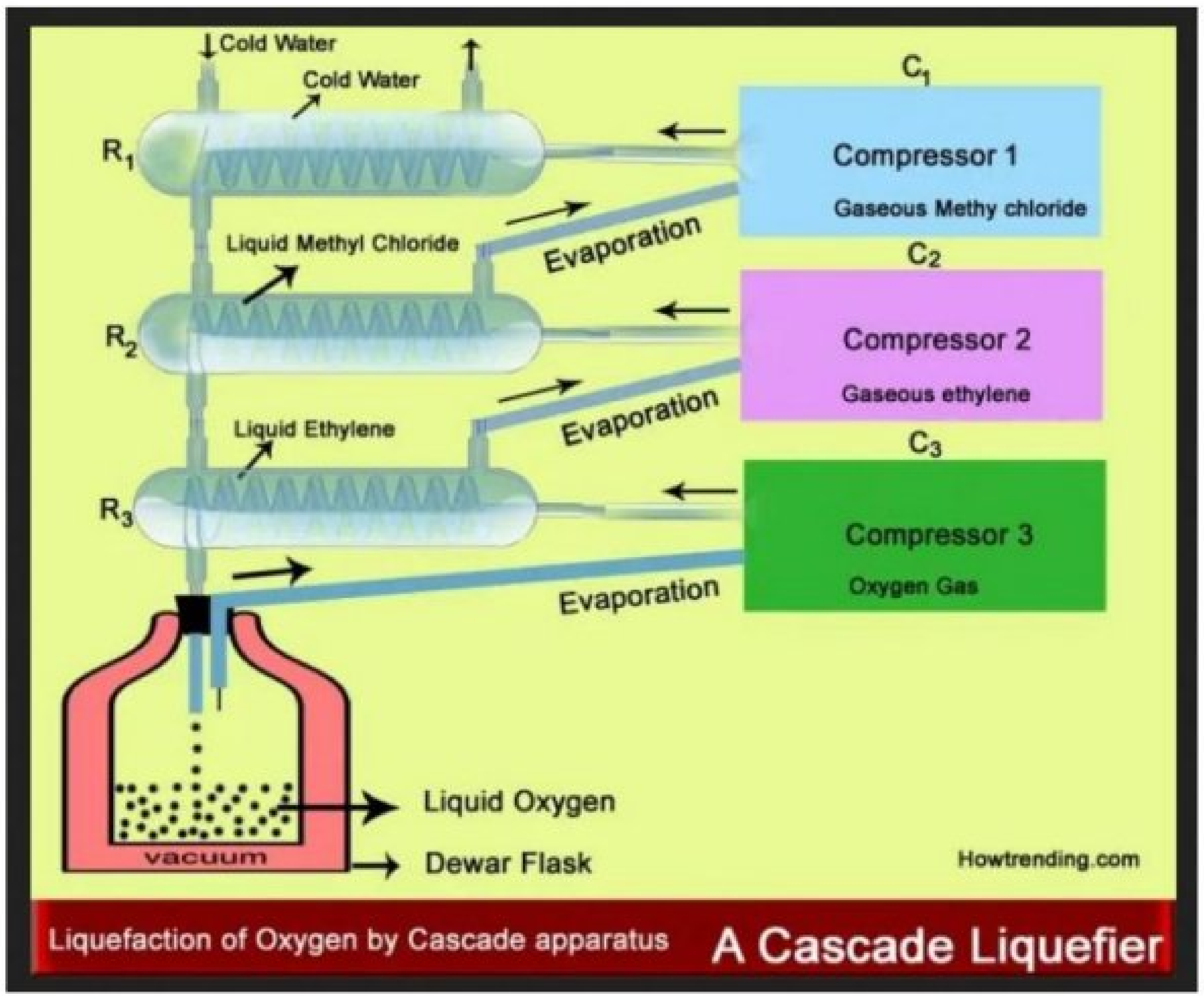


Fig: A Cascade Liquefier

Construction:

1. In this apparatus, three compressors C_1, C_2, C_3 are used to fulfill the requirement of sufficient pressure. Also, the C_1, C_2, and C_3 have a suction side which is used during the process.
2. Three condensers R_1, R_2, R_3 are used, into which three refrigerants cold water, Methyl chloride, and ethylene are used to get the desired result.
3. The Liquid oxygen is collected in the last, into a Dewar flask.

Principle: This apparatus work on two principles.

1. The first, Principle, compression of gases below its critical temperature resulting in a change to liquid.
2. The second is, producing cooling by the principle of evaporation of liquids.

Working:

- The gaseous methyl chloride (CH_3Cl) is pumped by the compressor C_1 into the spiral tube. The refrigerant in condenser R_1 surrounding this tube starts liquefying the methyl chloride.

- This is because the critical temperature of methyl chloride is 143°C, which is more than room temperature as well.

- Now the liquid methyl chloride comes in Condenser R_2 through the tube. Here one portion of condenser R_2 is connected with the suction side of compressor C_1.

- Here due to the evaporation of liquid methyl chloride in reduced pressure, more cooling as a result produced, and the temperature of condenser R_2 decreases more.

- The evaporated methyl chloride return back to the compressor C_1 through the suction side of the compressor.

- Now the gaseous ethylene (C_2H_4) is pumped by the compressor C_2 into the next spiral tube.

- Here the refrigerant, liquid methyl chloride which is achieved in the previous stage, surrounding the tube which contains gaseous ethylene, starts to convert this gas into liquid ethylene.

- This is because the critical temperature of ethylene is around 9.2°C.

- Now, this liquid ethylene comes in Condensor R_3, and one portion of R_3 condenser is connected with the suction side of compressor C_2.

- Here evaporation of liquid ethylene takes place in reduced pressure like in the previous stage, and the evaporated ethylene return back to the compressor C_2 through the suction side of the compressor.

- Therefore, due to the evaporation process more cooling is produced into the condenser R_3, which is more than the cooling that we achieved in Condenser R_2.

- This cooling has a temperature of around −160°C.

- Now, the oxygen (which is in gaseous form) is pumped by the compressor C_3 into the next spiral tube.

- Here, due to the very low temperature inside the Condenser R_3 the oxygen gas into the spiral tube starts converting into liquid and later collected into a Dewar flask.

- This is because the critical temperature of oxygen gas is around −118°C.

- Here, likewise the previous stages, the evaporated oxygen return back to the compressor C_3 through the suction side of the compressor.

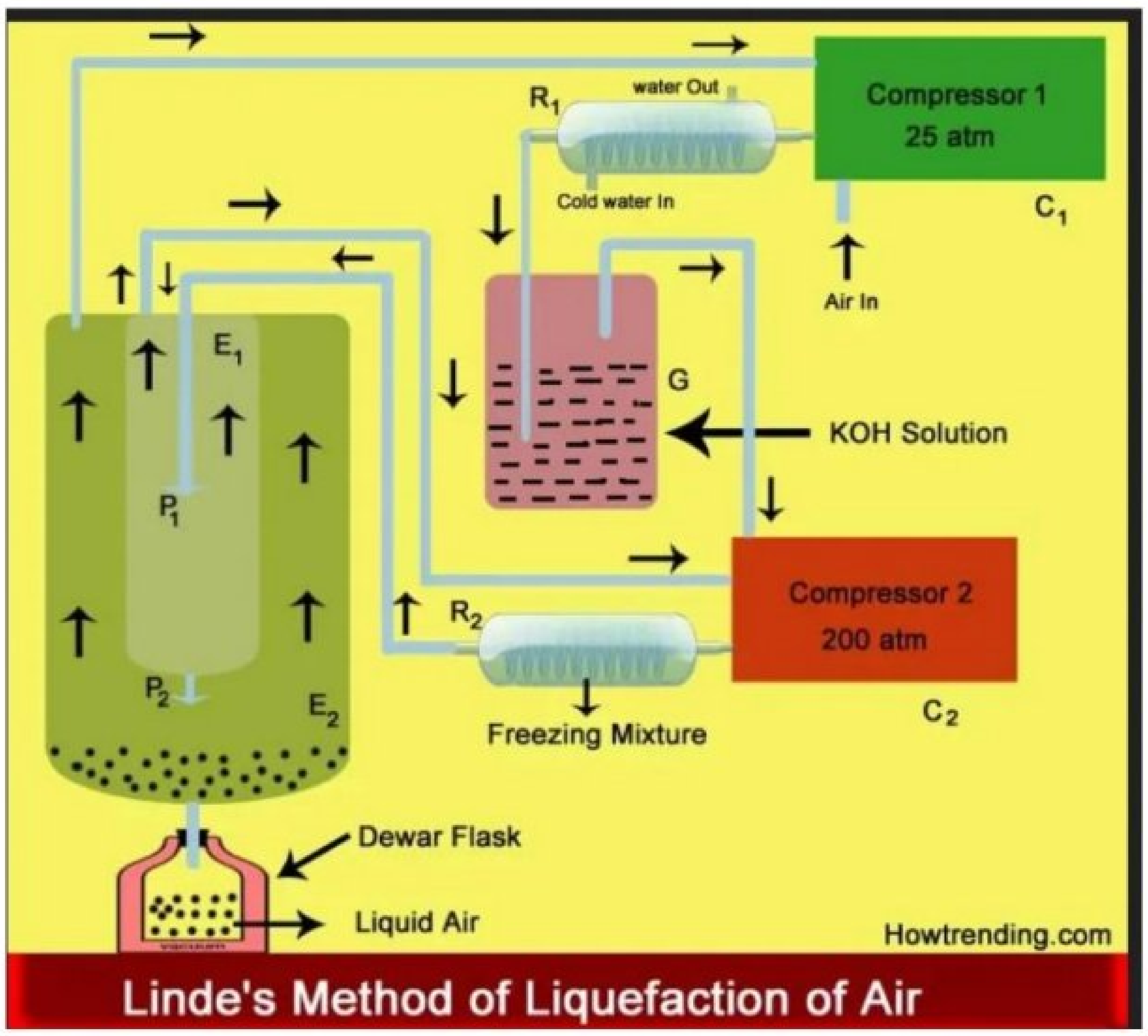
- If we continue this cascade system, we can liquefy air and other gases like Nitrogen, etc.

Limitation: By this system, we cannot liquefy the gases that have very low critical temperatures, such as Hydrogen (T_c around −240 °C) and Helium (T_c around −267.8 °C).

Linde's Method of liquefaction of gases.

The Hampson-Linde cycle or the Linde's liquefaction process is used by coupled with regenerative cooling and the Joule Thomson effect.

By this method, we can easily liquefy air, and many other gases too.



Linde's Method of Liquefaction of Gases

By this figure, you can understand that liquefaction of air or those gases that have a low value of critical temperatures is hard, as compared to those that have high critical temperature values.

Construction:

1. In this method, two compressors C_1 at (25 atm pressure) and C_2 (200 atm pressure) are used.
2. Heat exchangers R_1 and R_2 are used into which cold water and a freezing mixture is used as a refrigerant.
3. A Liquid solution of KOH (Potassium Hydroxide) that is required to get pure air.
4. Two chambers E_1 and E_2, and P_1 and P_2 are the two small nozzles.
5. At last, the liquid air is collected into a Dewar flask.

Principle: Linde's process of liquefaction is work on the principle of the **Joule Thomson effect** coupled with **regenerative cooling**.

Working:

1. The air is pumped at a pressure of 25 atm into the spiral tube. The air gets cooled after passing through the R_1 heat exchangers. Here the gas becomes cool because of cool water inside the R1 heat exchangers. This cooled air then passes through a liquid solution of Potassium hydroxide (KOH).

2. The reason for the use of the KOH solution is that air contains many gases and water vapours too. To separate air from water vapours this solution is used, and also this solution absorbs CO_2 gas from the air. After this, the air further moves in the second compressor C_2.

3. In the C_2 compressor, the air is pumped at a pressure of 200 atm into the next spiral tube. Now the gas becomes cool again, after passing through the second heat exchanger R_2. Here the gas-cooled because of the Freezing mixture inside the R_2 heat exchangers.

4. Now the temperature of this air decreases to around −20°C (253K). Then this pre-cooled air is allowed to expand through nozzle P_1 in a chamber E_1 and suffers the Joule Thomson effect. Due to this effect, more cooling is produced into the chamber E_1, and pressure reduces to about 50 atm.

5. This cooled air then returns back to the compressor C_2 and where it is again pumped at a pressure of 200 atm into the spiral tube. This air again suffers the Joule Thomson effect, and more cooling is produced in chamber E_1.

6. Repeating some cycles of this process, more and more cooling is produced in chamber E_1. After getting sufficient temperature, the cooled air is allowed to expand through nozzle P_2 in chamber E_2 and again suffers the Joule Thomson effect, and pressure reduces to about 1 atm.

7. Now the temperature decreases to around −188°C(85K) in chamber E_2 and the air gets liquefied. This liquefied air is collected into the Dewar flask.

8. Also, in chamber E_2 the un-liquefied air is returned back to the compressor C_1, this further cooled the air, and where it is again pumped at a pressure of 25 atm into the spiral tube.

The Liquefaction of Helium (Claude's method)

Helium is the only substance which means fluid at temperatures below -259ºC (4K) and its inversion point is much lower than that of Hydrogen namely around -233ºC(40K). The boiling point of Helium is just around -267ºC 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** (By, the use of an expansion turbine).

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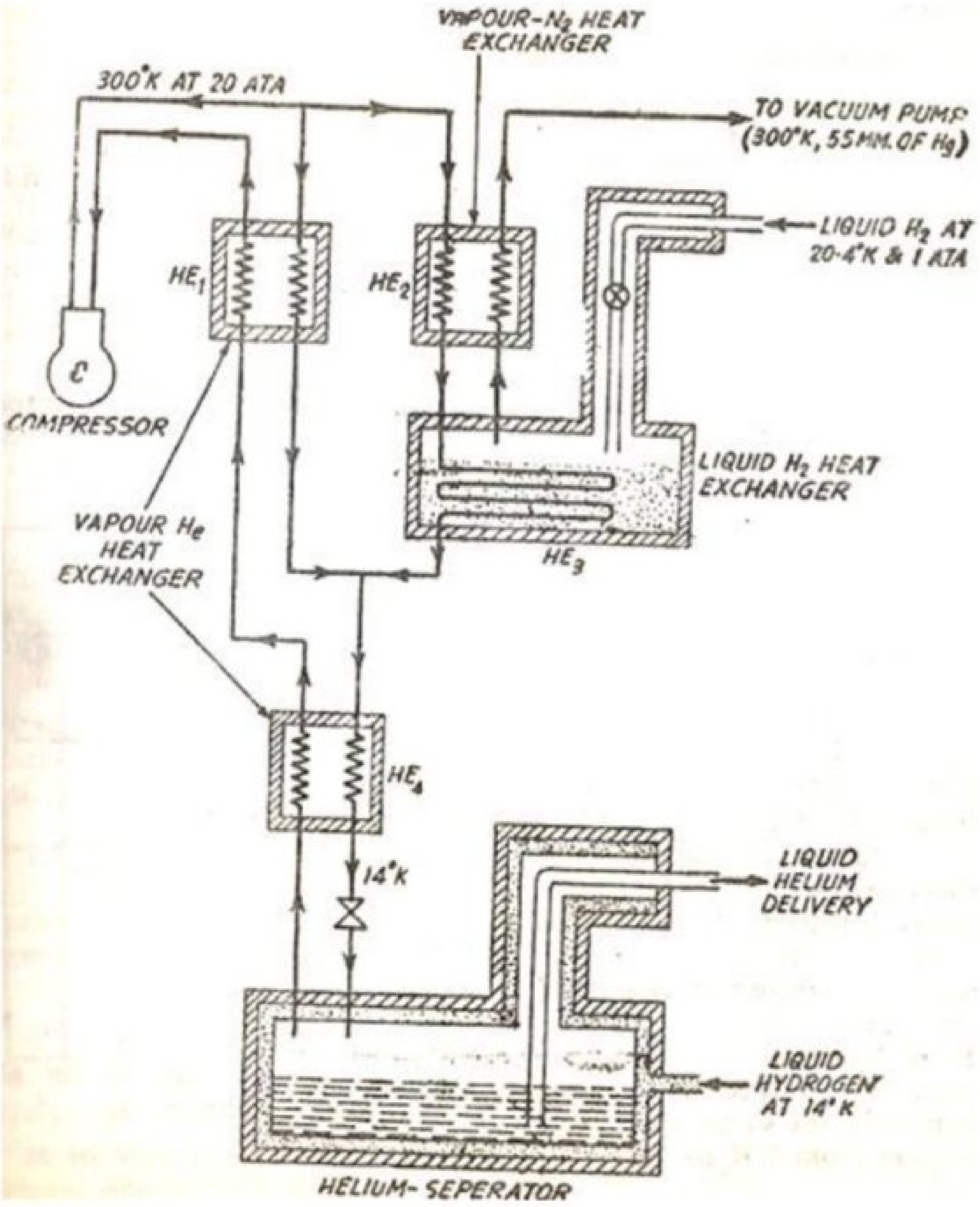

Working:

- 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 paths.

- The first part is cooled in the heat exchanger labelled HE1 with the help of Helium vapours
- The other part passes through the heat exchanger HE2 to be cooled with Hydrogen vapours.
- Both these streams combine to be passed through the liquid Hydrogen heat exchanger HE3
- Then again getting cooled in HE4 by Helium vapours.
- 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

Though the process described in the above section is generic in nature, in actual practice there are two main isotopes of Helium used for liquefaction namely H4 and H3 and there is a slight difference between the properties of the two in terms of their boiling point, critical temperature and so forth. The properties talked about earlier are those of H4 while the boiling point of H3 is even one degree lower.

Liquid Helium is used extensively for use in superconducting magnets which need to be cooled to extremely low temperatures during their use, that in turn are used in several fields such as say for Magnetic Resonance Imaging and Nuclear Magnetic Resonance.

Platinum Resistance Thermometer (PRT)

The Platinum Resistance Thermometer uses platinum for determining the temperature. It works on the principle of positive temperature coefficient of resistance that is 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 of platinum resistance Thermometer:

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.1). To measure change in resistance, Wheatstone bridge is used. Two long extension leads form one arm of Wheatstone bridge (fig.2).

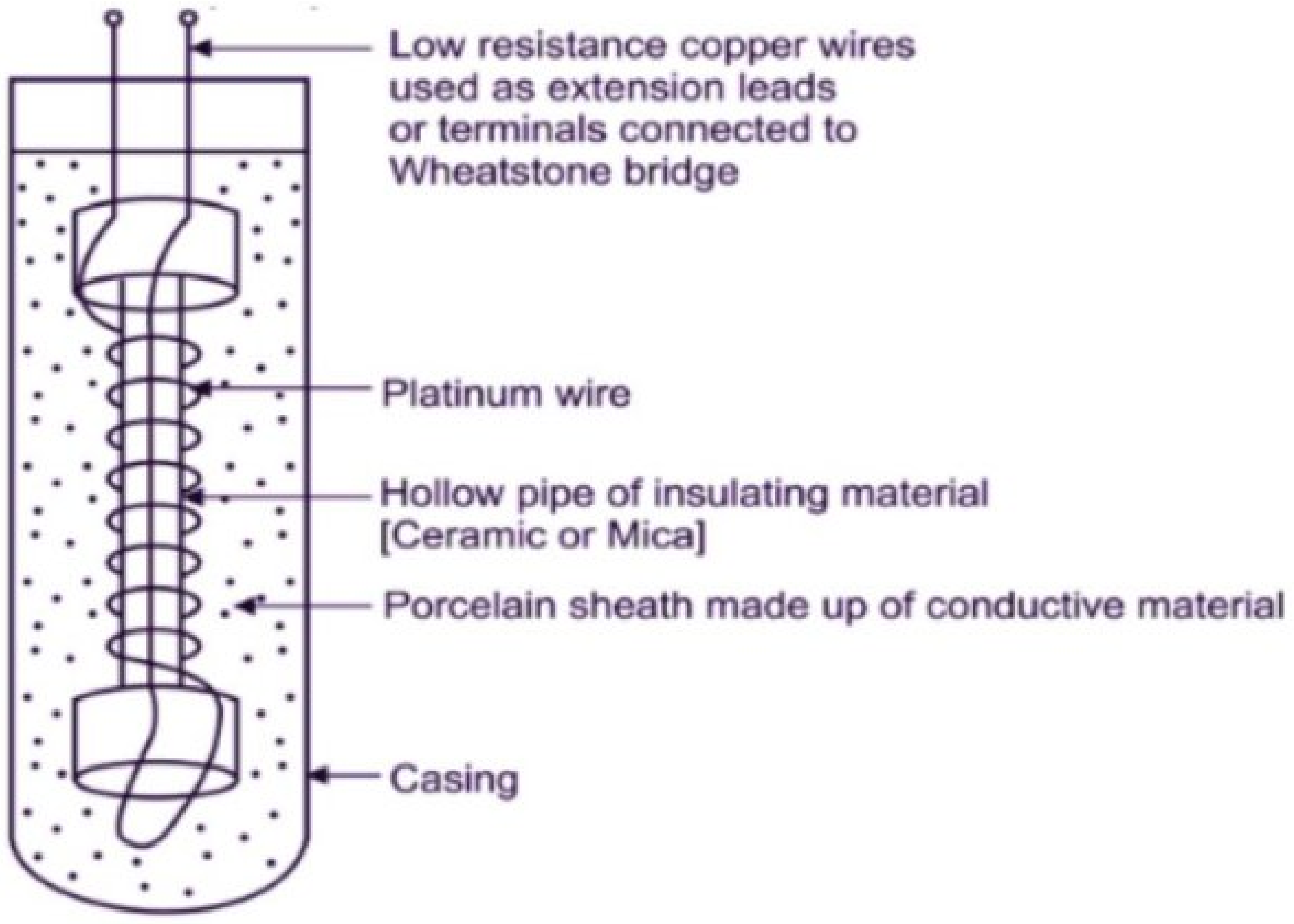

Fig.1: Platinum Resistance Thermometer

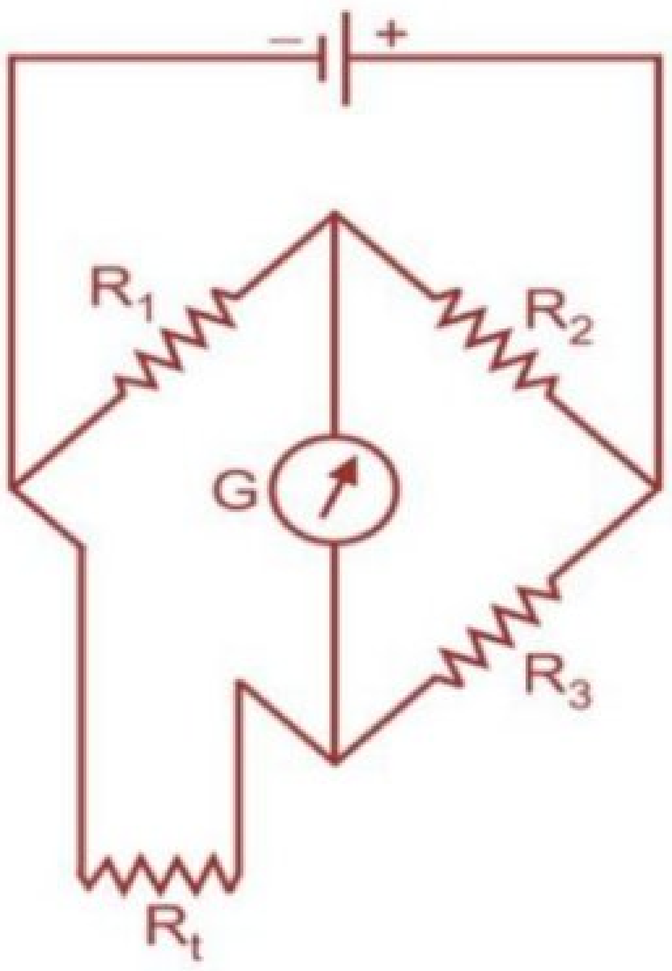

Fig2: PRT Wheatstone bridge

Working of platinum resistance Thermometer:

When platinum resistance Thermometer subjected to temperature variation, the wheatstone bridge gets unbalanced due to change in resistance R_t of platinum resistance. This makes the pointer move over circular scale of galvanometer, which is directly calibrated to give measured value of temperature.

Advantages of Platinum Resistance Thermometer

- 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.
- **high accuracy (0.01 °C),**
- The platinum gives stable value of resistance at the given temperature.
- Chemically inert

Disadvantages of Platinum Resistance Thermometer

- The thermometer gives the slow response.
- The melting point of the thermometer is 1800°C. But when platinum measures the temperature higher than 1200°C they start evaporating.

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1. In Joule Thomson experiment Temperature changes from 100ºC to 150ºC for pressure change of 20 MPa to 170 MPa. Calculate Joule Thomson Coefficient.

Given:

T1=100+273=373 K T2=150+273=423 K , P1=20Pa P2=170 pa

change in temperature from T2- T1 (K) = 50 K

change in pressure from P1 to P2 (Pa) = 150MPa

JTC = dT / dP = 50/150M =1/3 µK/Pa