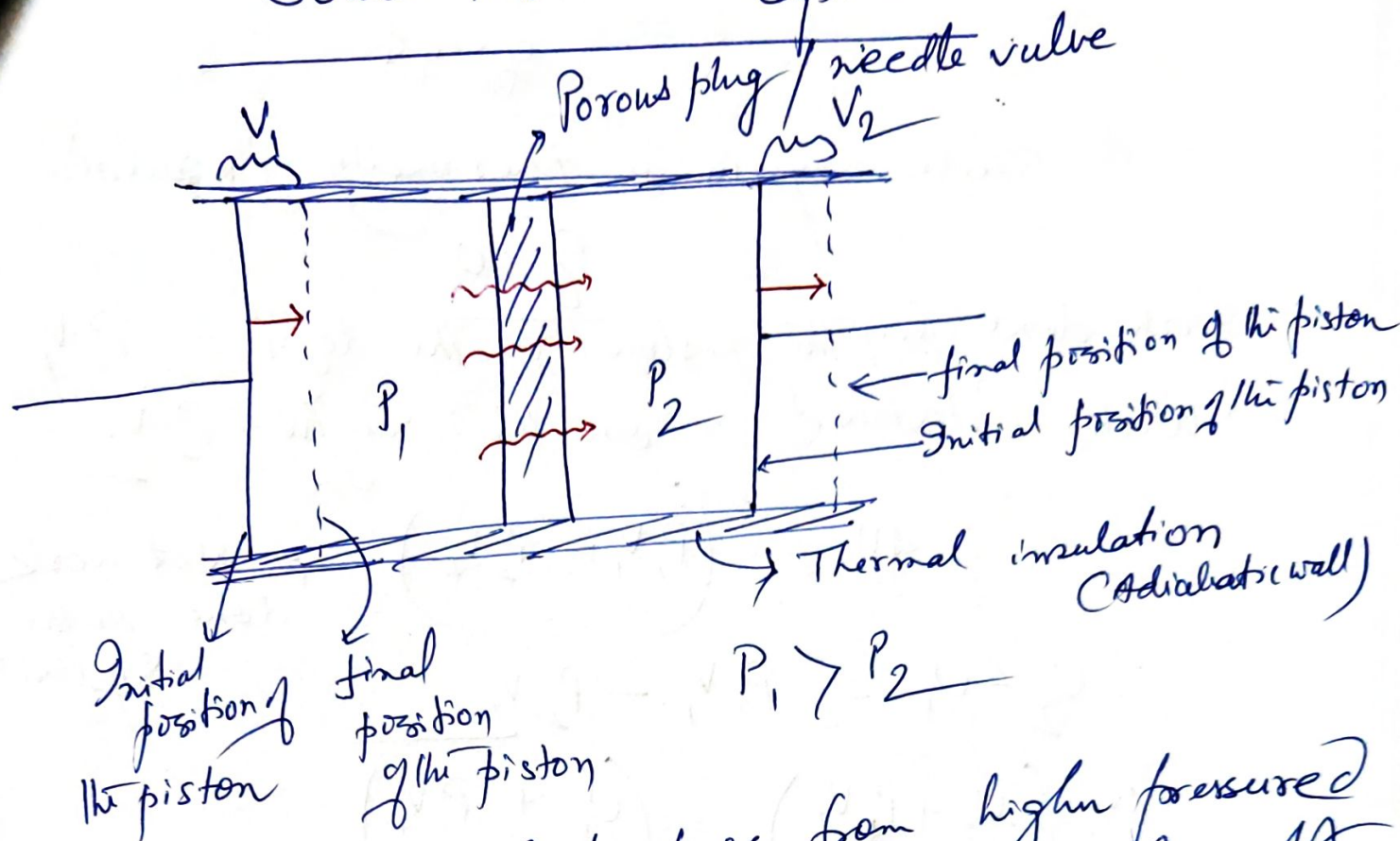


Joule-Thomson Expt :

(11)



Gas is allowed to pass from high pressure left compartment to the lower pressure right compartment through the porous plug.

In order to maintain the same pressure of the two compartments same (as P_1 in LH & P_2 at RH compartments), there will be compression (decrease in vol.) in left compartment by an amount V_1 & increase in vol. in right compartment by an amount of V_2 .

It is seen that for most of the ordinary temp. range, temp of the gas which passed from higher pressure to lower

pressure, decreases. \Rightarrow Joule-Thomson cooling effect.

As whole system is thermally insulated,
 $q = 0$.

Work done by the piston on the left = $P_1 V_1$

Work obtained on the right = $P_2 V_2$

$$\therefore \Delta U = (P_1 V_1 - P_2 V_2) \neq \text{Net work done on the system.}$$

$$\therefore U_2 - U_1 = P_1 V_1 - P_2 V_2$$

$$U_1 + (U_2 + P_2 V_2) = (U_1 + P_1 V_1)$$

$$\therefore H_2 = H_1 \Rightarrow \Delta H = 0$$

[Isoenthalpic process]

change in temp with pressure under
isoenthalpic condition:

Joule-Thomson coefficient: $\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H$

As dP is $(-)$; $\mu \rightarrow (+)$ if dT is $(-)$

$\mu \rightarrow (-)$, if dT is $(+)$.

At ordinary temps, most of the gases cooled down
passing to lower pressure through the
porous plug. Exception: H_2 & He

$\mu \rightarrow (-)$ at ordinary temp.

$$H = f(P, T)$$

$$dH = \left(\frac{\partial H}{\partial P} \right)_T dP + \left(\frac{\partial H}{\partial T} \right)_P dT$$

Here, $dH = 0$.

$$\therefore \left(\frac{\partial H}{\partial T} \right)_P dT = - \left(\frac{\partial H}{\partial P} \right)_T dP$$

$$\therefore \left(\frac{\partial T}{\partial P} \right)_H = - \frac{\left(\frac{\partial H}{\partial P} \right)_T}{\left(\frac{\partial H}{\partial T} \right)_P} = - \frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T$$

$$\boxed{\text{Joule Coeff}} \quad \eta = - \frac{1}{C_p} \left(\frac{\partial U}{\partial V} \right)_T$$

$$\therefore \boxed{\mu_{JT} = - \frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T}$$

Since, $H = U + PV$

$$\mu = - \frac{1}{C_p} \left(\frac{\partial U}{\partial P} \right)_T - \frac{1}{C_p} \left[\frac{\partial(PV)}{\partial P} \right]_T$$

For ideal gas, $\left(\frac{\partial U}{\partial P} \right)_T$ & $\left[\frac{\partial(PV)}{\partial P} \right]_T = 0$.

\therefore For ideal gas, $\mu_{JT} = 0$: Neither heating nor cooling

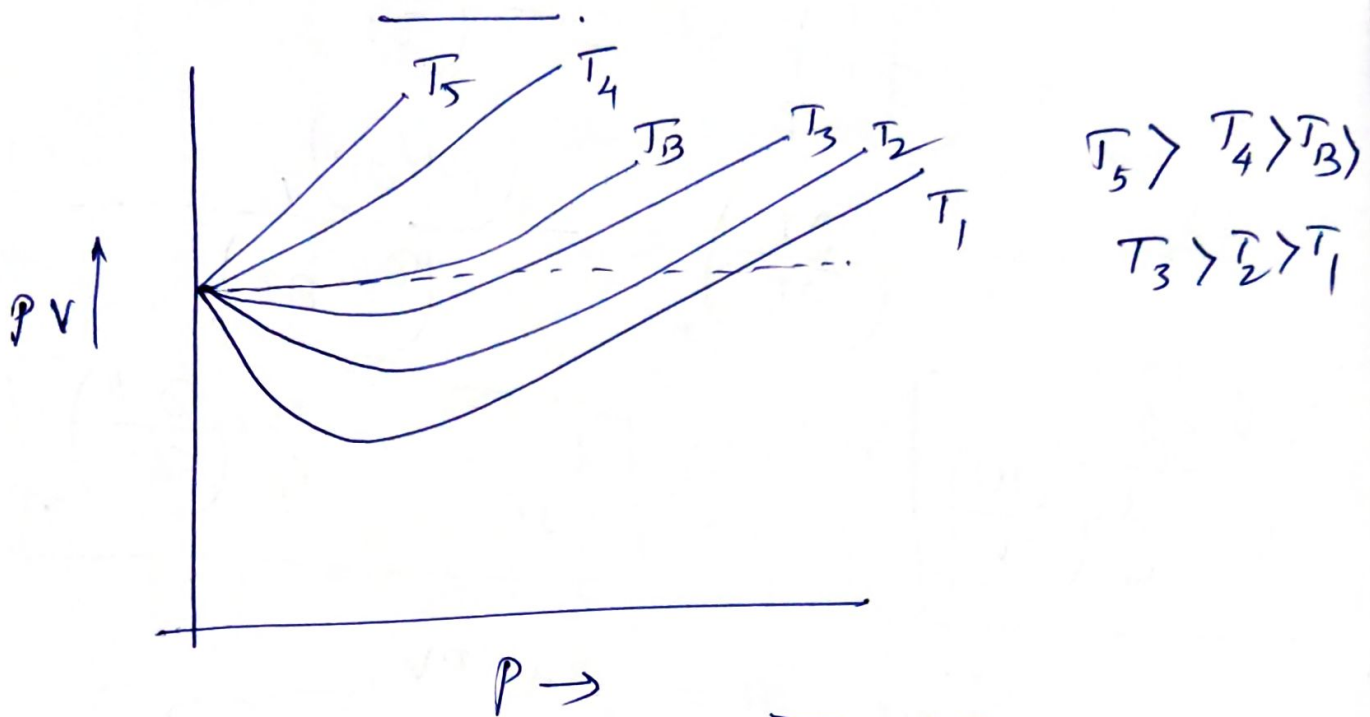
For real gas:

$$\mu_{JT} = - \frac{1}{C_p} \left[\left(\frac{\partial U}{\partial V} \right)_T \cdot \left(\frac{\partial V}{\partial P} \right)_T \right] - \frac{1}{C_p} \left[\frac{\partial(PV)}{\partial P} \right]_T$$

always (-)

always (+): cooling effect

Thus, the magnitude of the second term will decide if μ_{JT} will be (+) (re. cooling effect) or (-) (re. heating effect)



At lower temp range, $\left[\frac{\partial(PV)}{\partial P} \right]_T = (-)$

Thus overall $\mu_{JT} \rightarrow (+)$ at lower temp range.

(As both terms will be positive)
 But at higher temp range, Cooling at lower temp range

$$\left[\frac{\partial(PV)}{\partial P} \right]_T = (+)$$

In this situation, if numerical value of second term exceeds that of 1st term,

Overall $\mu_{JT} \rightarrow (-)$: Heating at higher temp range

For every gas, there is an intermediate temp, when $\mu_{JT} = 0$: (15)

Inversion Temperature (T_i)

At T_i ; $\mu_{JT} = 0$, i.e. 1st term and second term cancel each other at T_i .

If the expt. temp is $< T_i$: $\mu_{JT} \Rightarrow (+)$: cooling
- - - - - $> T_i$: $\mu_{JT} \Rightarrow (-)$: Heating

T_i : He 40K (-233°C)

H_2 -51°C (202K)

N_2 : 621K (348°C)

Thus, for He & H_2 , T_i is much lower than the normal atmospheric temp.

Thus with these two gases under normal temp J.T. expt. heating is observed.

More about inversion temp (T_i)

Temp. at which $\mu_{JT} = 0$, is called the inversion temp. of that particular gas.

$$\text{Now: } \mu_{JT} = -\frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T$$

Another thermodynamic eqⁿ of state:

$$\left(\frac{\partial H}{\partial P} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_P + V$$

$$\begin{aligned} \therefore \mu_{JT} &= -\frac{1}{C_p} \left[-T \left(\frac{\partial V}{\partial T} \right)_P + V \right] \\ &= \frac{V}{C_p} \left[\frac{T}{V} \left(\frac{\partial V}{\partial T} \right)_P - 1 \right] \end{aligned}$$

$$= \frac{V}{C_p} [T\alpha - 1]$$

$$\left[\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \alpha \right]$$

Coeff of thermal expansion

When $T = T_i$, $\mu_{JT} = 0$.

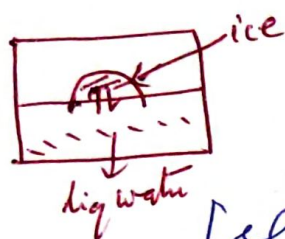
$$\therefore T_i \alpha_i - 1 = 0$$

$$\therefore \boxed{T_i = \frac{1}{\alpha_i}}$$

\Rightarrow \therefore Isobaric expansibility of a gas at the temp T_i .

change in phase

When two phases of same component are at equilibrium at a fixed T and pressure, then we can write:



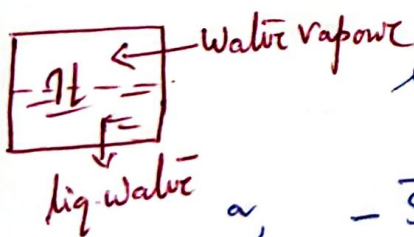
$$\mu_I = \mu_{II}$$

$\mu \Rightarrow$ Chemical potential of the component
I & II: at two different phases.

[e.g. suppose liq water is in eqm with solid ice].

(by changing T/P)

Now, if this eqm is slightly disturbed, and again sufficient time is allowed to restore a new eqm, then change in chemical potential in both the phases will be equal.



$$d\mu_I = d\mu_{II}$$

$$\left[\begin{array}{l} dG = -SdT + VdP \\ \text{Per mole:} \\ d\mu = -\bar{S}dT + \bar{V}dP \end{array} \right]$$

$$\therefore -\bar{S}_I dT + \bar{V}_I dP = -\bar{S}_{II} dT + \bar{V}_{II} dP$$

$$\therefore \left(\frac{dP}{dT} \right) = \frac{\bar{S}_{II} - \bar{S}_I}{\bar{V}_{II} - \bar{V}_I} = \frac{\Delta \bar{S}}{\Delta \bar{V}} = \frac{\Delta \bar{H}}{T \cdot \Delta \bar{V}}$$

$\Delta \bar{S}$ & $\Delta \bar{V}$: change in molar entropy or volume while going from phase I to II.

Clapeyron Eqn.

Now, during vapourisation process:

Now, during vapourisation process:

$$\frac{dS}{dT} \frac{dP}{dT} = \frac{\Delta \bar{H}}{T(\bar{V}_g - \bar{V}_l)}$$

$$\text{As, } \bar{V}_g \gg \bar{V}_l : \quad \frac{dP}{dT} = \frac{\Delta \bar{H}}{T \cdot \bar{V}_g}$$

Considering vapour to behave like an ideal gas:

(3)

$$\bar{V}_g = \frac{RT}{P}$$

$$\therefore \left[\frac{dP}{dT} = \frac{\Delta \bar{H} \cdot R \cancel{TP}}{T \cdot RT} = \frac{\Delta \bar{H} \cdot P}{RT^2} \right]$$

$$\therefore \frac{dP}{P} = \frac{\Delta \bar{H}}{R} \cdot \frac{dT}{T^2}$$

Specific
 $\Delta \bar{H} \Rightarrow$ latent
 heat of
 evaporation.

Integrating, $\ln \left(\frac{P_2}{P_1} \right) = -\frac{\Delta \bar{H}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

$$\therefore \left[\ln \left(\frac{P_2}{P_1} \right) = \frac{\Delta \bar{H}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right]$$

(P_1, T_1) and (P_2, T_2) are the two points along the co-existence curve (liq-vap.).

These eq^{ns} are known as Clausius-Clapeyron eqⁿ.

$$\ln P = -\frac{\Delta \bar{H}}{R} \left(\frac{1}{T} \right) + C$$

For liq-gas transition: $\Delta \bar{H}$: specific latent heat of vaporisation

For, solid-gas transition: $\Delta \bar{H}$: specific latent heat of sublimation.

If we consider the liquids at their boiling temp (T_B), then the pressure P will be one atmosphere ($P=1$)

$$\therefore \frac{\Delta \bar{H}}{T_B} = R \underline{\text{const}} \Rightarrow (\Delta \bar{S}_{\text{vap}})_{\text{at } T_B} \Rightarrow \text{const}$$

$\Delta \bar{H} \Rightarrow$ Specific/molar latent heat of vapourisation.

Trautman had made this important generalisation from experimental observation and stated that:

"the ratio of the molar heat of vapourisation to the boiling point is a constant for simple or non-associated liquids and the constant is approximately 21° (Cal $K^{-1} \text{mol}^{-1}$)"

i.e. molar entropy change on vapourisation at the boiling temp is constant.

\Rightarrow Trautman's rule.

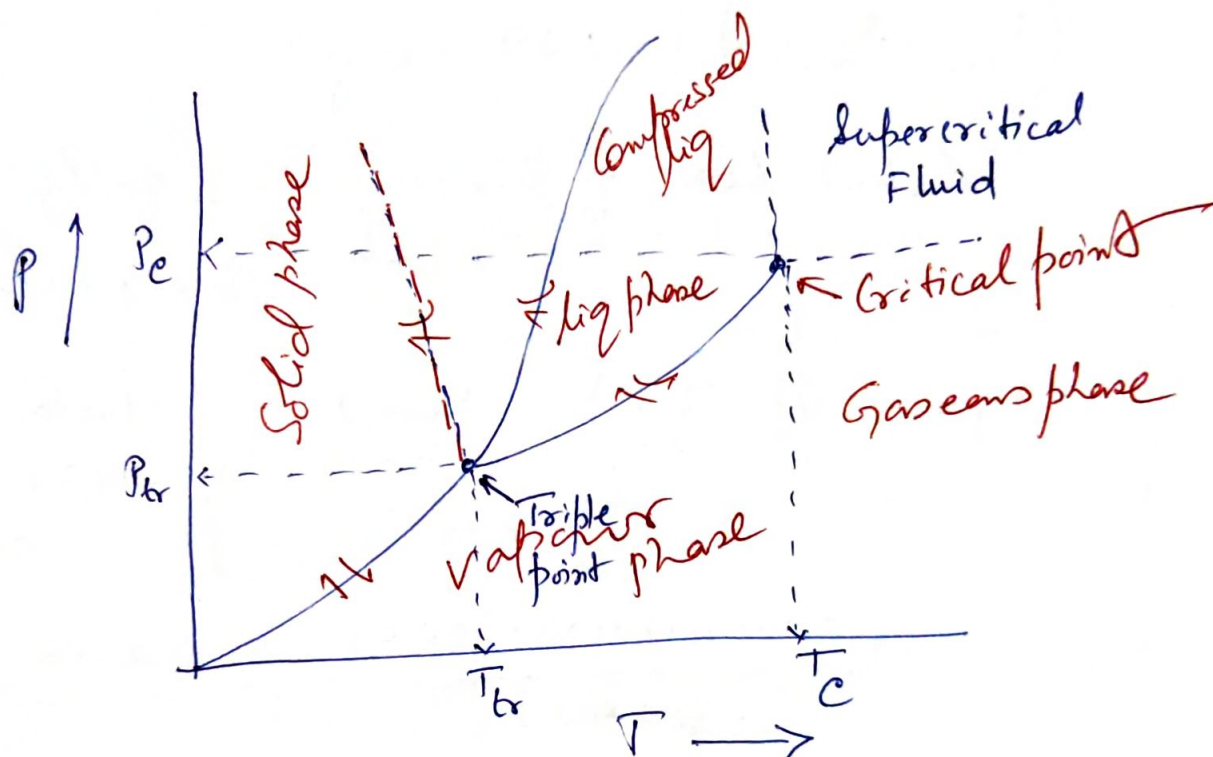
$$\left(\Delta \bar{S}_{\text{vap}} \right)_{\text{at } T_B} \approx 10.5 R \Rightarrow \approx 21 \text{ Cal } K^{-1} \text{mol}^{-1} \approx 85-88 \text{ J } K^{-1} \text{mol}^{-1}$$

	$B.P. (^\circ C)$	$1/T_B$
n-Hexane	68.7	20.28
n-Heptane	94.4	20.61
n-Octane	125.6	20.96

Also valid for

Xylene, Toluene, CS_2 , benzene, HCl , HBr (not HF).

However, Trouton's rule fails for liquids which are associated (like H_2O , alcohols) and also in the case of low-boiling or high boiling liquids: (like: O_2 , N_2 , H_2 , NH_3 etc.)



A typical Phase diagram (The dotted line gives the anomalous behavior of water)

Calculate the freezing temp of water if the pressure be increased by 1 atm.
(Latent heat of fusion = 80 cal/g)

$$\frac{\Delta P}{\Delta T} = \frac{L}{T (\bar{V}_{ice} - \bar{V}_{water})}$$

$$(\bar{V}_{ice} - \bar{V}_{water}) = 0.09 \text{ cc.g}^{-1}$$

Latent heat of freezing = -80 cal/g
 $= -80 \times 4.2 \times 10^7 \text{ erg/g}$

$$\therefore \Delta T = \frac{\Delta P \cdot T (\bar{V}_{ice} - \bar{V}_{water})}{L_{\text{freezing}}}$$

$$= \frac{13.6 \times 981 \times 273 \times 0.09}{-80 \times 4.2 \times 10^7}$$

$$= -0.008^\circ \text{C}$$

Thus, water will freeze at -0.008°C at 2 atm pressure.

$$\left. \begin{aligned} &1 \text{ atm} \\ &= 13.6 \times 981 \times 76 \\ &\quad \downarrow \text{CGS unit} \\ &\text{density of Hg (g cc}^{-1}\text{)} \\ &1 \text{ atm} \Rightarrow 76 \text{ cm of Hg column.} \end{aligned} \right\}$$

Under what pressure will water boil at 98°C ? (7)
 ($L_{\text{evap}} = 536 \text{ cal/g}$)

$$\frac{dp}{dT} = \frac{L P}{RT^2}$$

$$\therefore \Delta P = \frac{L \cdot P}{RT^2} \cdot \Delta T = \left[\frac{18 \times 536}{2 \times 373^2} \times 760 \times (-2) \right] \text{ mm}$$

$$\left[\begin{array}{l} 1 \text{ atm} \Rightarrow 760 \text{ mm of pressure} \\ R \approx 2 \text{ cal K}^{-1} \text{ mol}^{-1} \end{array} \right]$$

$$\left(18 \times 536 \right) \Rightarrow \text{Latent heat of evaporation: } \underline{\text{cal mol}^{-1}}$$

$$\therefore \Delta P = -54 \text{ mm.}$$

Then, at 98°C , water will boil under 706 mm of pressure.

The densities of α - and β -sulphur are 2 and 1.95 respectively at their transition temp 96°C . The transition temp changes by 0.036° for every atmosphere rise in pressure. Find out the heat of transition: