⑥. **Clapeyron Equation:**

From thermodynamics, we know that for any pure substance in a single phase, such as, liquid or gaseous water, the variation in free energy is given by.

$$dG = v\,dp - S\,dT \qquad \cdots \cdots (i)$$

For a pure substance present in two phases A and B at a pressure P and temperature, T the condition of equilibrium is

$$\overline{G}_B = \overline{G}_A$$

$$or,\ \Delta G = 0 \qquad \cdots \cdots (ii)$$

where $\overline{G}_A$ is the free energy per mole of the substance in the initial phase A and $\overline{G}_B$ is the free energy per mole in the final phase B.

If the temperature of the system is changed to $T+dT$, then the pressure of the system will change to $P+dP$ to maintain the equilibrium. The relationship between dT and dP can be derived from thermodynamics as—

Let the free energy per mole of the substance in phase A at the new temperature and pressure be $\overline{G}_A + d\overline{G}_A$ and that in phase B be $\overline{G}_B + d\overline{G}_B$. Since the two phases are still in equilibrium, hence

$$\overline{G}_A + d\overline{G}_A = \overline{G}_B + d\overline{G}_B \qquad \cdots (iii)$$

According to eqⁿ (i), $d\overline{G}_A = V_A\,dP - S_A\,dT \quad \cdots (iv)$

and $\quad d\overline{G}_B = \overline{V}_B dP - S_B\,dT \qquad \cdots \cdots (v)$

Since $\quad \overline{G}_A = \overline{G}_B$

Hence, from eqⁿ (iii) $d\overline{G}_A = d\overline{G}_B \quad \cdots (vi)$

$$V_A\,dP - S_A\,dT = V_B\,dP - S_B\,dT \qquad \cdots (vii)$$

$$or,\ \frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A}$$

$$or,\ \frac{dP}{dT} = \frac{\Delta S}{\Delta V} \qquad \cdots \cdots \cdots (viii)$$

~~Eqⁿ (viii) is~~ where ΔS and ΔV are the change in

entropy and volume are respectively. When 1 mole of the substance passes from the initial phase A to be final phase B.

If 'q' is the heat exchanged reversibly per mole of the substance during the change of phase at temperature T, then the change of entropy (ΔS) in this process is given by $\Delta S = \dfrac{q}{T}$.

Hence, $\dfrac{dP}{dT} = \dfrac{q}{T.\Delta V}$ — — — — (ix)

or, $\dfrac{dP}{dT} = \dfrac{q}{T(V_B - V_A)}$ — — — (x)

The eqⁿ (x) is known as **clapeyron Equation** and given change in pressure accompanying the change in temperature dT or vice versa when two phases of a pure substance are in equilibrium with each other.

Clausius – Clapeyron Equation :

The clapeyron equation, when applied to the liquid-vapour or solid-vapour equilibrium, with the assumption that the volume of the liquid and solid phase is negligible as compared to vapour phase which behaves as an ideal gas, is called the Clausius – Clapeyron equation.

If the temperature is not too near the critical temperature, then $V_g \gg V_L$ or, V_s

and $V_g = \dfrac{RT}{P}$

With this simplification we can write from eqⁿ (x),

$$\dfrac{dP}{dT} = \dfrac{\Delta H}{T V_g} = \dfrac{\Delta H}{T} \times \dfrac{P}{RT} = \dfrac{P \, \Delta H}{RT^2}$$

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

$\left[\begin{array}{l} q = \Delta H = \text{molar} \\ \text{heat of vaporisa-} \\ \text{tion} \end{array} \right]$

— — — (xi)

This differential equation may be employed if the changes in temperature and pressure are small.

Integrated Form of Clausius–Clapeyron Equation:

Assuming that ΔH (molar enthalpy of vaporization / molar enthalpy of sublimation) remains constant to small temperature variations, integration of equation (xi) yields,

$$\int \frac{dP}{P} = \frac{\Delta H}{R} \int \frac{dT}{T^2}$$

or, $\ln P = -\frac{\Delta H}{R} \cdot \left(\frac{1}{T}\right) + c$ — — — — (xii)

or, $\log P = -\frac{\Delta H}{2.303\,R}\left(\frac{1}{T}\right) + c'$ — — — — (xiii)

where c and c' are integration constants.

Again, $\int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta H}{R} \cdot \int_{T_1}^{T_2} \frac{dT}{T^2}$

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

or, $\ln \frac{P_2}{P_1} = \frac{\Delta H}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$ — — — — (xiv)

If ΔH is known, vapour pressure at a desired temperature can be calculated from the knowledge of single value of vapour pressure at a given temperature.

Numerical Problems:

1. At 373.6 K and 372.6 K the vapour pressures of water are 1.018 and 0.982 atms respectively. Calculate the heat of vapourisation of water.

Ans.
$T_1 = 372.6\,K$ $R = 8.314 \ JK^{-1}$

$T_2 = 373.6 \ K$ $\Delta_v H = ?$

$P_1 = 0.982 \ atm$

$P_2 = 1.018 \ atm$

According to Clausius–Clapeyron equation,

$$\log\left(\frac{P_2}{P_1}\right) = \frac{\Delta_v H}{2.303\,R} \times \left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

or, $\log \frac{1.018}{0.982} = \frac{\Delta_v H}{2.303 \times 8.314} \times \frac{1}{372.6 \times 373.6}$

$$\Delta H = 41676.13 \text{ J/mol.}$$
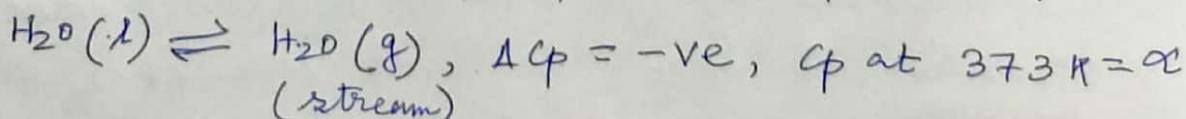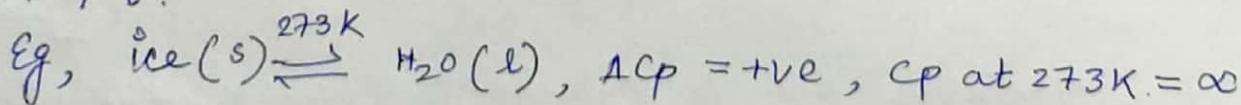$$= 41.676 \text{ KJ/mol.}$$

Phase Transition:

Many substances exist in more than one solid forms differing in crystal structures which are quite stable thermodynamically over certain range of temperature and pressure. This phenomenon is called polymorphism. In the case of elements, this property of polymorphism is called __allotropy__. Due to change in T and P, one form (phase) may change or undergo transition into the other form. This process in which a new phase appears without taking place of a chemical reaction is called _phase transition_.

a) First - order Phase Transitions:

These are the transitions which are accompanied by transfer of heat between the system and the surroundings ($q_p \neq 0$). The heat capacity $C_p = \left(\frac{\partial H}{\partial T}\right)_p$ may be +ve or -ve. during transition from low temperature phase to high temperature phase. Since, at the equilibrium transition temperature, latent heat is involved. without change of temperature, $C_p = \frac{dq_p}{dT}$ is infinite. Further, in these transitions, there is change in the enthalpy and volume of the system, i.e., $\Delta v \neq 0$, $\Delta H \neq 0$.

Eg, $ice (s) \underset{}{\overset{273K}{\rightleftharpoons}} H_2O (l)$, $\Delta C_p = +ve$, C_p at $273K = \infty$

$H_2O (l) \rightleftharpoons H_2O (g)$, $\Delta C_p = -ve$, C_p at $373K = \infty$
   (stream)

The clapeyron equation is applicable to the first order transitions.

In the first order transitions, there is change in

the Gibbs free energy and a finite change in the volume and entropy at constant pressure. Since the latter quantities are first derivatives of the free energy, such transitions are accompanied by discontinuity in the first derivatives, i.e., the slopes of the plots of μ against P or T are different on either side of the transition.

Also, $\left(\dfrac{\partial \mu}{\partial T}\right)_P = -\bar{s}$ and $\bar{s}$ of a pure substance is always +ve about $0K$, therefore, 'μ' of each phase decreases with increasing T.

Further, $S(g) > S(l) > S(s)$ so that,

$$\left(-\dfrac{\partial \mu}{\partial T}\right)_{gas} > \left(-\dfrac{\partial \mu}{\partial T}\right)_{liq} > \left(-\dfrac{\partial \mu}{\partial T}\right)_{solid}$$

The change of μ of the solid, liquid and gas phase of a pure substance with temperature at constant pressure can be shown in the figure. T_m is the melting point and T_b is the boiling point of the substance.
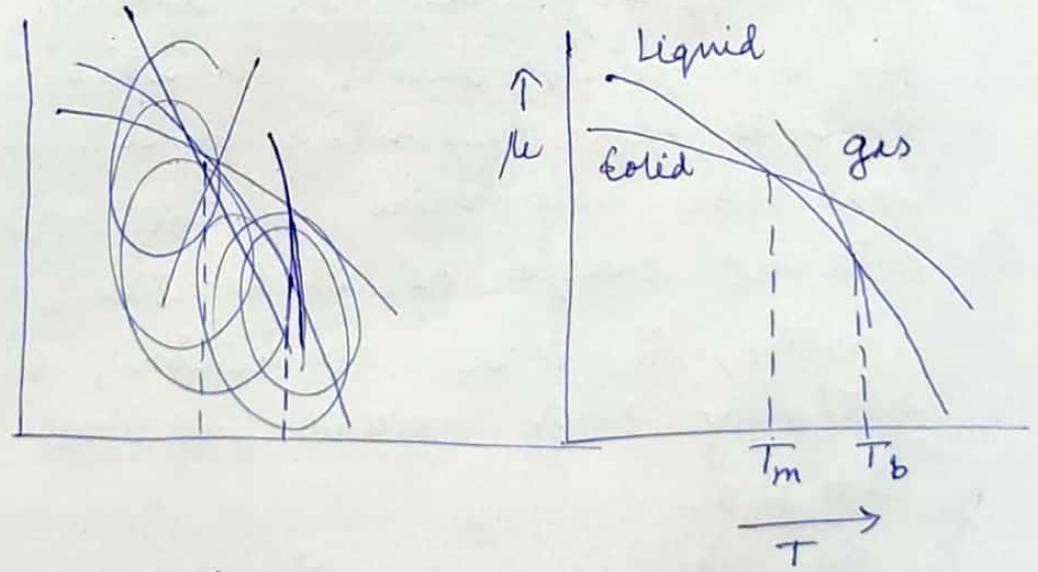
Variation of μ with T in first order phase transition at eqm of pure substance at constant pressure.