In phase rule, it is assumed that equilibrium is not influenced by other variables like electrical, magnetic & gravitational forces. (19)

PHASE DIAGRAM :

It is a diagram giving condition of equilibrium between various phases of a substance in a closed system in absence of air.

Phase Equilibria involving Phase Transition :

It governs curves in phase diagram.

~~Clap~~ Clapeyron Equation :

In a system of a pure substance, if several phases are present in equilibrium under a set of conditions, there is always a possibility of transition of the substance from one phase to another by altering any of the variables of the system.

This equation represents thermodynamic relation between the change of pressure with change of temperature of a system at equilibrium.

Let us consider an equilibrium between 2 phases α & β of a pure substance at constant Temperature & Pressure.

$$\text{Phase } (\alpha) \rightleftharpoons \text{Phase } (\beta)$$

At equilibrium,

$$\Delta G = G^{\beta} - G^{\alpha} = 0 \quad \text{i.e.} \quad G^{\beta} = G^{\alpha}$$

Let Temperature & Pressure are changed to $T + dT$

& $P+dP$ such that α & β are still at equilibrium (20)

$G^\alpha = G^\beta$ i.e. $(G+dG)^\alpha = (G+dG)^\beta$

$\therefore dG^\alpha = dG^\beta$

$dG = -SdT + VdP$

$-S^\alpha dT + V^\alpha dP = -S^\beta dT + V^\beta dP$

$(S^\beta - S^\alpha) dT = (V^\beta - V^\alpha) dP$

$$\frac{dP}{dT} = \frac{S^\beta - S^\alpha}{V^\beta - V^\alpha} = \frac{\Delta S}{\Delta V}$$

$$\boxed{\frac{dP}{dT} = \frac{\Delta S}{\Delta V}}$$

S^β & S^α are entropies of pure substances in different phases.

For 1 mole, V can be replaced by V_m & S by S_m, where V_m & S_m represents molar volume & molar entropy.

for 'n' moles, volume $= V$

for '1' mole, volume $= \frac{V}{n} = V_m$ = Molar volume = volume of 1 mole of substance.

Similarly, S_m.

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T \Delta V_m}$$

For ~~kg~~ 1 mole of substance, total volume $= \Delta H_m$ (have 'M' molecular weight)

For 1g of substance, total volume $= \frac{\Delta H_m}{M} = \Delta H$

$$\frac{dP}{dT} = \frac{1}{T(V_m^\beta - V_m^\alpha)}$$

These are general thermodynamic relations applicable (2.) to all phase transitions of a pure substance.

$$\frac{dP}{dT} = \frac{\Delta H_m}{T \Delta V_m} \quad (1.)$$

For complete change, integrate this equation from limits T_1 to T_2 & P_1 to P_2.

$$\int_{P_1}^{P_2} dP = \frac{\Delta H_m}{\Delta V_m} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\boxed{P_2 - P_1 = \frac{\Delta H_m}{\Delta V_m} \ln \frac{T_2}{T_1}} \quad -(2)$$

This can be done if we know Temperature & Pressure dependence of ΔH_m & ΔV_m (usually not available). In above case, ΔH_m & ΔV_m are assumed to be independent of Temperature & Pressure.

Eq. (2.) is used for processes involving condensed phases.

Let us consider different equilibria:

(1.) Liquid - vapour equilibrium:

Vaporization process $\quad liq \rightleftharpoons vap.$

$$\boxed{\frac{dP}{dT} = \frac{\Delta H_{vap,m}}{T(V_m^v - V_m^l)}} \quad -(3.)$$

V_m^v = Molar Volume of vapour phase of the substance

V_m^l = Molar Volume of liquid phase of the substance

$V^v > V^l$

$\Delta H_{vap,m}$ = Molar change in enthalpy of vaporization = Positive value.

from eq. (3), $\frac{dP}{dT}$ = positive for liquid to vapour phase transition of a substance.

(2.) **Solid - Liquid Equilibrium:**

(Fusion Process) solid ⇌ liquid

$$\boxed{\frac{dP}{dT} = \frac{\Delta H_{fus,m}}{T(V_m^l - V_m^s)}}$$

V_m^s = molar Volume of solid phase of a substance

V_m^l = Molar Volume of liquid phase of a substance.

$V_m^l > V_m^s$ (for most substances)

$\Delta H_{fus,m}$ = Change in molar enthalpy of fusion = Positive

So $\frac{dP}{dT}$ = positive for solid to liquid phase transition of most of the substances

For water, $V_m^l < V_m^s$ (as water in form of ice is ~~more~~ less dense as ice occupies more space because of hydrogen bonding & hence has high volume as ice).

$\frac{dP}{dT}$ = Negative for water.

(3.) **Solid - ~~liq~~ Vapour Equilibrium:**

(Sublimation Process) solid ⇌ vapour

$$\frac{dP}{dT} = \frac{\Delta H_{sub,m}}{T(V_m^v - V_m^s)}$$ = Positive for all substances.