

## Clausius - Clapeyron equation:

When two phases are in equilibrium, their chemical potential must be equal.

$$\text{i.e. } \mu_{\alpha}(p, T) = \mu_{\beta}(p, T) \longrightarrow \textcircled{1}$$

where  $\alpha$  and  $\beta$  are two phases in eqm.

By solving this eqn  $\textcircled{1}$  for pressure in terms of temp<sup>r</sup>, we can get an eqn for the phase boundaries.

$dT$ ,  $p$  and  $T$  be changed infinitesimally so that two phases  $\alpha$  and  $\beta$  remains in eqm. So, the change in chemical potential in the two phases must be equal.

$$\therefore d\mu_{\alpha} = d\mu_{\beta} \longrightarrow \textcircled{II}$$

$$\Rightarrow V_{\alpha, m} \cdot dp - S_{\alpha, m} \cdot dT = V_{\beta, m} \cdot dp - S_{\beta, m} \cdot dT$$

where,  $V_{\alpha, m}$  and  $V_{\beta, m}$  are molar vol<sup>m</sup> of  $\alpha$  &  $\beta$ .  
 $S_{\alpha, m}$  and  $S_{\beta, m}$  are molar entropies of  $\alpha$  &  $\beta$ .

$$\left\{ \begin{array}{l} \therefore d\mu = v dp - s dT \\ \Delta S = \frac{q}{T} \\ q \text{ is heat exchanged.} \end{array} \right.$$

$$\therefore (V_{\beta, m} - V_{\alpha, m}) \cdot dp = (S_{\beta, m} - S_{\alpha, m}) dT$$

$$\Rightarrow \boxed{\frac{dp}{dT} = \frac{\Delta S_{\text{trans}}}{\Delta V_{\text{trans}}}}$$

$$\Rightarrow \boxed{\frac{dp}{dT} = \frac{q}{T \cdot \Delta V}} \textcircled{III}$$

This is Clapeyron eqn and is applicable to any phase eqm of any pure substance for liquid  $\rightleftharpoons$  vapour,  $q = \Delta_{\text{vap}} H$ .

$$\therefore \text{by } \textcircled{III} \Rightarrow \boxed{\frac{dp}{dT} = \frac{\Delta_{\text{vap}} H}{T \cdot \Delta V}}$$

### Solid-Liquid Boundary:

Melting (fusion) is accompanied by molar enthalpy series,  $\Delta_{\text{fus}} H$  and occurs at a temp  $T$ .

The molar entropy of melting is thus  $\frac{\Delta_{\text{fus}} H}{T}$ .

$$\therefore \frac{dP}{dT} = \frac{\Delta_{\text{fus}} H}{T \cdot \Delta_{\text{fus}} V}$$

### Liquid-Vapour Boundary:

$$\frac{dP}{dT} = \frac{\Delta_{\text{vap}} H}{T \cdot \Delta_{\text{vap}} V} \longrightarrow \textcircled{0}$$

Molar vol<sup>m</sup> of a gas is so much greater than that of liquid we can write,  $\Delta_{\text{vap}} V \approx V_m(g)$ .

For perfect gas,

$$\Delta_{\text{vap}} V \approx V_m(g) = \frac{RT}{P}$$

$$\text{Eqn } \textcircled{0} \Rightarrow \frac{dP}{dT} = \frac{\Delta_{\text{vap}} H}{T} \times \frac{P}{RT}$$

$$\Rightarrow \frac{1}{P} \cdot \frac{dP}{dT} = \frac{\Delta_{\text{vap}} H}{RT^2}$$

$$\Rightarrow \boxed{\frac{d(\ln P)}{dT} = \frac{\Delta_{\text{vap}} H}{RT^2}} \text{ this is called } \textcircled{11}$$

Clausius eq<sup>n</sup>.

### Integrated form: Clausius-Clapeyron eq<sup>n</sup>:

Assuming that  $\Delta_{\text{vap}} H$  remains constant over a small range of temp<sup>r</sup>, we have from eq<sup>n</sup>  $\textcircled{11}$ ,

$$\int d(\ln P) = \frac{\Delta_{\text{vap}} H}{R} \int \frac{dT}{T^2}$$

$$\Rightarrow \ln P = - \frac{\Delta_{\text{vap}} H}{R} \times \frac{1}{T} + I \quad \left\{ I \text{ is integration constant} \right\}$$

↳ (iii)

Integrating eqn (iii) between limits of pressure  $P_1$  and  $P_2$  corresponding to  $T_1$  and  $T_2$ , we get,

$$\int_{P_1}^{P_2} d(\ln P) = \frac{\Delta_{\text{vap}} H}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\Rightarrow \ln \frac{P_2}{P_1} = - \frac{\Delta_{\text{vap}} H}{R} \left[ \frac{1}{T} \right]_{T_1}^{T_2}$$

$$\Rightarrow \ln \frac{P_2}{P_1} = - \frac{\Delta_{\text{vap}} H}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\Rightarrow \ln \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}} H}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\Rightarrow \boxed{\log \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}} H}{2.303 R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]}$$

This is the integrated form of clayperon eqn and is called Clausius-Clayperon eqn.