Day 30

→ Aliovalent incorporation –

Parent / Host material is interacting with an atmosphere

equilibrium of $M^{+1}X^{-1}$ at a particular temperature in contact with X_2 gas.

$a_{X_2} \sim P_{X_2}$ $\quad M^{2+}X^{2-}$ (X → oxygen)

(activity) (partial pressure) → can be controlled over several orders of magnitude

$$\text{Resistance} \propto \frac{1}{\text{conductivity}}$$

$[N] \geq |e| \mu_N(T,P)$

↓

is orders of magnitude

Possible defects : $[V_x^{\cdot}]$, $[M_i^{\cdot}]$, $[h^{\cdot}]$, $[V_M^{'}]$, $[X_i^{'}]$, $[e']$

so $[V_x^{\cdot}] + [M_i^{\cdot}] + [h^{\cdot}] = [V_M^{'}] + [X_i^{'}] + [e']$

Electroneutrality condition

$$\frac{1}{2}X_2 \longrightarrow [X_i^{'}] + [h^{\cdot}] \quad (K_{X_i}) \quad \text{(*)}$$

$$M_M^x + X_x^x \longrightarrow \frac{1}{2}X_2 + V_x^{\cdot} + [e'] + M_M^x \quad (K_{X_2})$$

2nd reaction is reverse of incorporation

$$K_{x_1} = \frac{[X_i'][h^\cdot]}{\sqrt{P_{x_2}}} \quad \text{And} \quad K_B = [e'][h^\cdot]$$

$$[h^\cdot][X_i'] = K_{x_1} P_{x_2}^{1/2}$$

→ Brouwer approximation –

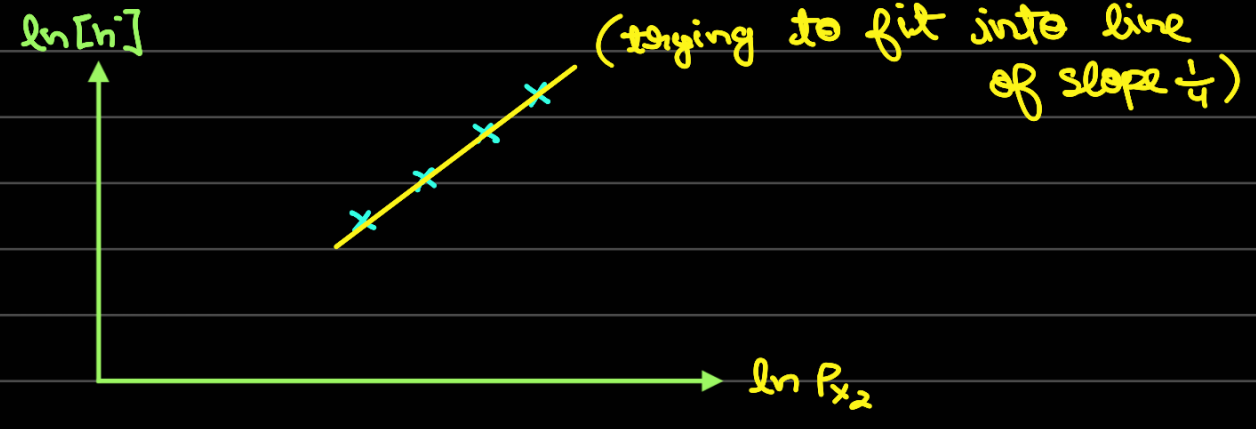
T, P : only 1 +ve defect and 1 – ve defect are the majority

$$[V_x^\cdot] + [m_i^\cdot] + [h^\cdot] = [V_m'] + [X_i'] + [e']$$

Assumed majority

[Brouwer regime] → we have 9 in this case

So $[h^\cdot] = K_{x_1}^{1/2} P_{x_2}^{1/4}$



Cases : $[V_x^\cdot] = [V_m']$ (Schottky)

$[V_x'] = [X_i']$ (Anion Frenkel)

} does not depend on external parameter

$$[V_x^\cdot] = [e']$$

Brouwer regimes → N, I and P

✱ For high partial pressure of X_2 (oxidising atmosphere)

$$[h^{\cdot}][e'] = K_B$$

$$\Rightarrow [e'] = \frac{K_B}{[h^{\cdot}]}$$

Since $[h^{\cdot}] \propto P_{x_2}^{1/4} \Rightarrow [e'] \propto P_{x_2}^{-1/4}$

If $[h^{\cdot}]$ in I region where anion-Frenkel is active. So

$$[x_i'] = [V_x^{\cdot}]$$

$$[x_i'][V_x^{\cdot}] = K_{AF}$$

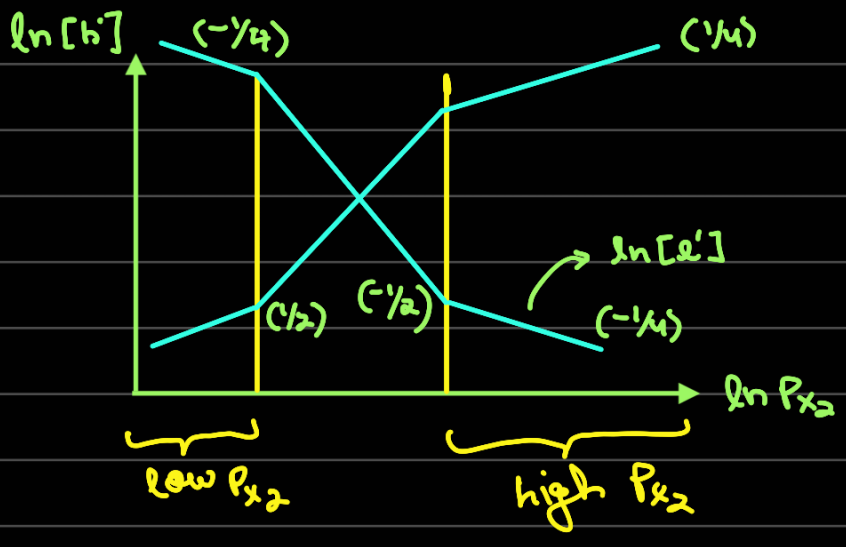
$$\Rightarrow [x_i'] = \sqrt{K_{AF}}$$

Now $[h^{\cdot}][x_i'] = K_{x_1} P_{x_2}^{1/2}$

↓ fixed

so $[h^{\cdot}] \propto P_{x_2}^{1/2}$

$[e'] \propto P_{x_2}^{-1/2}$



$$K_{x_2} = [e'][V_x^{\cdot}] P_{x_2}^{1/2} \Rightarrow [e'][V_x^{\cdot}] \propto P_{x_2}^{-1/2}$$

From Brouwer approximation, $[e'] \propto P_x^{-1/4}$