

Chemical equilibrium



$$K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \quad K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad K_x = \frac{x_C^c \cdot x_D^d}{x_A^a \cdot x_B^b}$$

In general, the equilibrium constant follows the equation.

$$K_a = \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} \quad \text{where } a_i = \frac{f_i}{f^\circ} \quad \text{where } f \rightarrow \text{fugacity}$$

$$\therefore K_p = \frac{\left(\frac{P_C}{P^\circ}\right)^c \cdot \left(\frac{P_D}{P^\circ}\right)^d}{\left(\frac{P_A}{P^\circ}\right)^a \cdot \left(\frac{P_B}{P^\circ}\right)^b} \quad \left| \begin{array}{l} \cancel{K_c = \frac{(C^\circ)^c \cdot (D^\circ)^d}{(A^\circ)^a \cdot (B^\circ)^b}} \\ \text{Same to} \end{array} \right. \quad \frac{(C_C)^c \cdot (C_D)^d}{(C_A)^a \cdot (C_B)^b}$$

$$P^\circ = 1 \text{ atm.}$$

$$\therefore K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\text{Now, } K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$$

$$= \frac{(n_C \cdot RT)^c \cdot (n_D RT)^d}{V^c \cdot V^d}$$

$$= \frac{(n_A RT)^a \cdot (n_B RT)^b}{V^a \cdot V^b}$$

$$= \frac{n_C^c \cdot n_D^d}{n_A^a \cdot n_B^b} \cdot \left(\frac{RT}{V}\right)^{(c+d)-(a+b)}$$

$$= \frac{(n_C)^c \cdot (n_D)^d}{(n_A)^a \cdot (n_B)^b} \cdot \left(\frac{RT}{V}\right)^{4n}$$

$$\Rightarrow K_p = \frac{x_A^c \cdot x_B^d}{x_A^a \cdot x_B^b} \cdot \left(\frac{RT}{V}\right)^{4n}$$

$$= K_x \cdot \left(\frac{RT}{V}\right)^{4n} = K_x \cdot (P)^{4n}$$

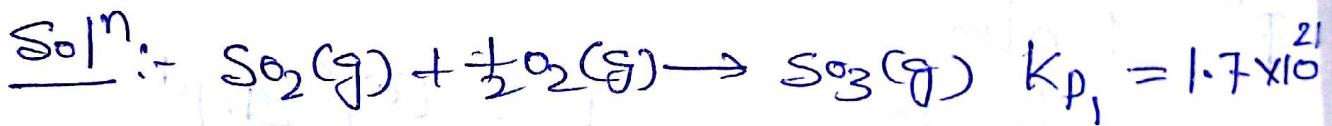
$$\boxed{K_p = K_c \cdot (RT)^{4n}} = K_c \cdot \left(\frac{c^o RT}{P^o}\right)^{4n}$$

Hence, $K_x \cdot \left(\frac{RT}{V}\right)^{4n} = K_c \cdot (RT)^{4n}$

$$\therefore \boxed{K_x = K_c \cdot (V)^{4n}}$$

* K_p for $S_0_2(g) + \frac{1}{2} O_2(g) \rightarrow S_0_3(g)$ is

1.7×10^{21} at 300 K. Calculate K_p and K_c for $2S_0_3 \rightarrow 2S_0_2 + O_2$



\therefore For the rxn

$$S_0_3 \rightarrow S_0_2 + \frac{1}{2} O_2 \therefore K_p = \frac{1}{1.7 \times 10^{21}}$$

$$\Rightarrow 2S_0_3 \rightarrow 2S_0_2 + O_2 \therefore K_p = \frac{1}{(1.7 \times 10^{21})^2}$$

$$= 3.46 \times 10^{-43}$$

Now, $K_p = K_c \cdot (RT)^{4n}$

Hence, $4n = 1$

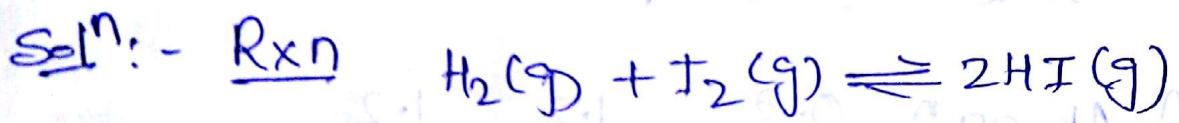
$$\therefore K_c = \frac{K_p}{RT} = \frac{3.46 \times 10^{-43}}{300 \times 0.082} = 1.4 \times 10^{-44}$$

$$R = 8.314 \text{ J. K}^{-1} \cdot \text{mol}^{-1}$$

$$= 1.987 \text{ cal. K}^{-1} \cdot \text{mol}^{-1}$$

$$= 0.082 \text{ lit-atm. K}^{-1} \cdot \text{mol}^{-1}$$

① A mixture containing 8.07 moles of H_2 and 9.08 moles of I_2 was heated at 448°C till eqⁿ was attained when 13.38 moles of HI was obtained. Calculate the eqⁿ. const. K_c .



Initial concn 8.07 9.08 0

Bqⁿ $(8.07-x) (9.08-x) 2x$

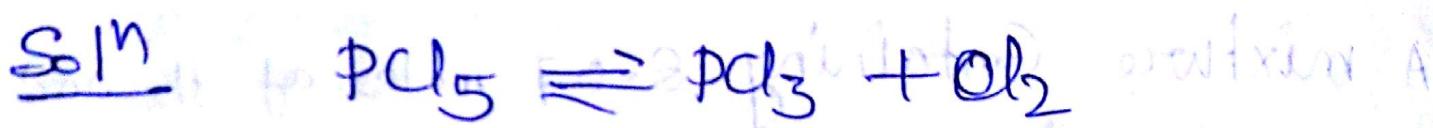
Now, $2x = 13.38 \text{ mole} \Rightarrow x = 6.69 \text{ mole}$

$\therefore \text{At eq}^n, [\text{H}_2] = \frac{8.07 - 6.69}{V} = 1.38 \text{ mol/lit}$

$[\text{I}_2] = \frac{9.08 - 6.69}{V} = 2.39 \text{ mol/lit}$

$\therefore K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(13.38)^2}{1.38 \times 2.39} = 54.279$

* 2 moles of PCl_5 was heated in a 2 litre flask at 250°C to establish the eqn, at which 60% PCl_5 was dissociated to PCl_3 and Cl_2 . Find out K_p .



Initially	2 moles	0	0
At eqn,	2 - 1.2	1.2	1.2 mol.

~~At~~ volume = 2 litr.

$$\therefore \text{Conc. At eqn} \quad \frac{0.8}{2} \quad \frac{1.2}{2} \quad \frac{1.2}{2}$$

$$\therefore K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(0.6 \times 0.6)}{0.4} = 0.9$$

$$\text{Now, } K_p = K_c (RT)^4$$

$$\begin{aligned} K_p &= 0.9 \times (0.082 \times 523)^4 \\ &= 385.9 \end{aligned}$$

$$K_p = \frac{P(\text{Cl}_2)^2}{P(\text{PCl}_5)}$$

Chemical equilibrium

Van't Hoff isotherm:-

$$dG = Vdp - SdT$$

$$dG_T = Vdp$$

$$\overline{dG}_T = \frac{RT}{P} dp$$

$$G = G^\circ + RT \ln P$$

$$\text{Hence, } \Delta G = \sum G_{\text{product}} - \sum G_{\text{reactant}}$$

$$= (c \cdot G_c^\circ + cRT \ln P_c + d \cdot G_d^\circ + dRT \ln P_d) \\ - (a \cdot G_a^\circ + aRT \ln P_a + b \cdot G_b^\circ + bRT \ln P_b)$$

$$= \Delta G^\circ + RT \ln \frac{P_c^c \cdot P_d^d}{P_a^a \cdot P_b^b}$$

$$\boxed{\Delta G = \Delta G^\circ + RT \ln K_p} \rightarrow ①$$

At equilibrium, $\Delta G = 0$.

$$\text{show: } \Delta G^\circ = -RT \ln K_p$$

$$\boxed{K_p = e^{-\frac{\Delta G^\circ}{RT}}} \quad \text{Reduction}$$

$$\frac{\Delta G^\circ}{T} = -R \ln K_p$$

$$\frac{d}{dT} \left(\frac{\Delta G^\circ}{T} \right) = -\frac{d}{dT} (R \ln K_p) \rightarrow ②$$

From Gibbs-Helmholtz eqn

$$\frac{d}{dT} \left(\frac{\Delta H^\circ}{T} \right) = - \frac{\Delta H^\circ}{T^2} \rightarrow ③$$

$$\therefore - \frac{\Delta H^\circ}{T^2} = -R \cdot \frac{d}{dT} \ln K_p$$

$$\int_{k_1}^{k_2} d \ln K_p = \int_{T_1}^{T_2} \frac{\Delta H^\circ}{R} \cdot \frac{dT}{T^2}$$

$$\Rightarrow \ln \frac{K_p 2}{K_p 1} = \frac{\Delta H^\circ}{R} \cdot \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

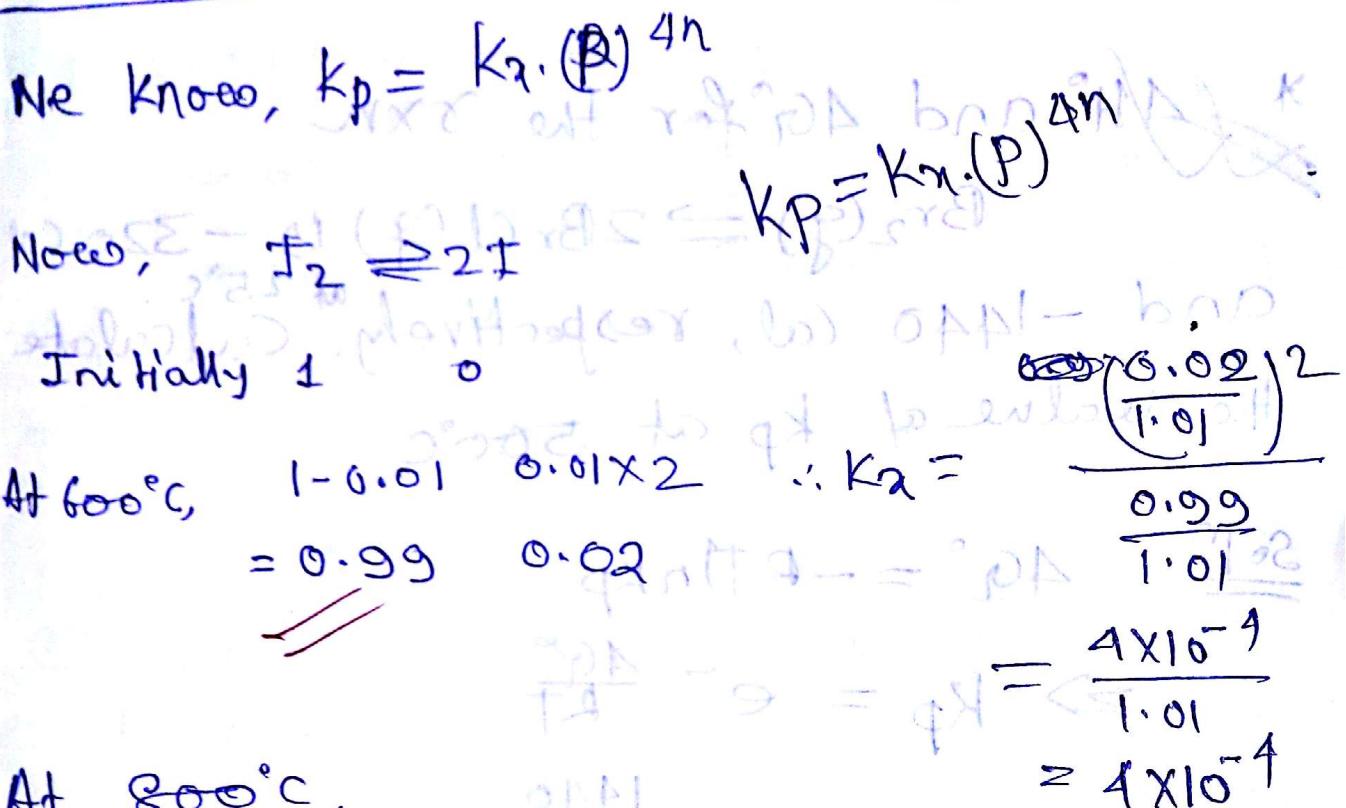
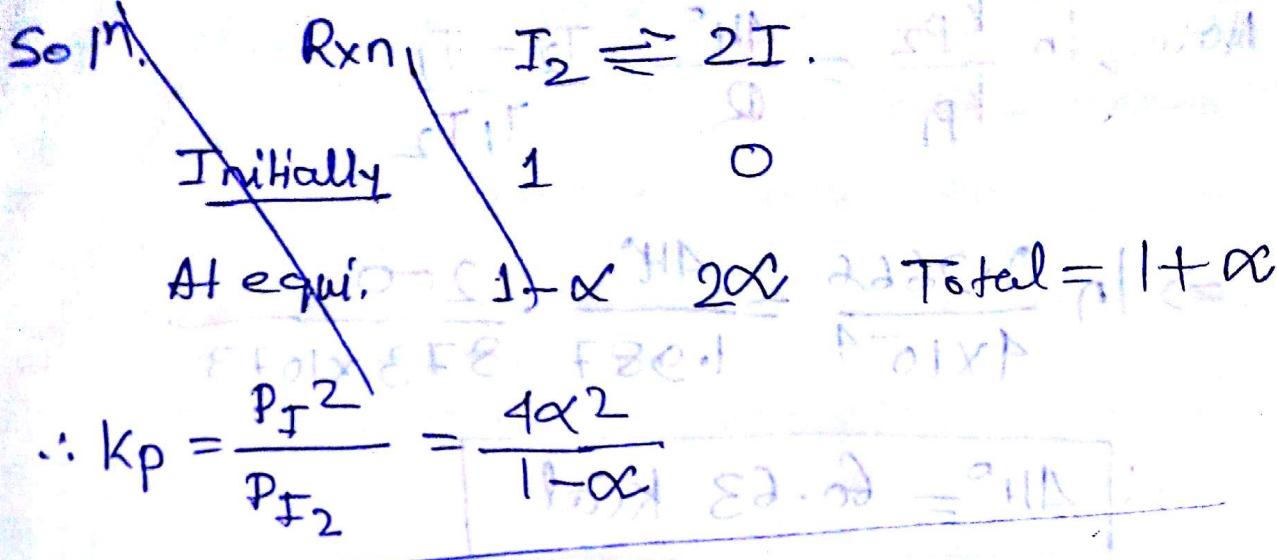
$$\boxed{\ln \frac{K_p 2}{K_p 1} = \frac{\Delta H^\circ}{R} \cdot \frac{T_2 - T_1}{T_1 T_2}}$$

$$\boxed{\ln \frac{K_C 2}{K_C 1} = \frac{\Delta U^\circ}{R} \cdot \frac{T_2 - T_1}{T_1 T_2}}$$

Van't Hoff Isotherm.

Q Gaseous I_2 at 1 atm. pressure is 1% dissociated into atoms at $600^\circ C$ and 25% dissociated at $800^\circ C$. Calculate ΔH° for the dissociation. Calculate ΔG° at $600^\circ C$.

$$\chi = 0.025$$



$$\therefore K_x = \frac{\left(\frac{0.50}{1.25}\right)^2}{\frac{0.75}{1.25}} = 0.26666$$

$$\therefore K_p = K_x \cdot (P)^{4n} = 4 \times 10^{-9}$$

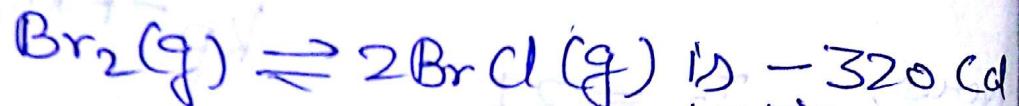
$$K_p_{800^\circ C} = K_x \cdot (P)^{4n} = 0.2666$$

$$\text{Now, } \ln \frac{K_P 2}{K_P 1} = \frac{4H^\circ}{R} \cdot \frac{T_2 - T_1}{T_1 T_2}$$

$$\Rightarrow \ln \frac{0.2666}{4 \times 10^{-9}} = \frac{4H^\circ}{1.987} \cdot \frac{200}{873 \times 1073}$$

$$\therefore 4H^\circ = 60.63 \text{ kcal}$$

~~* $4H^\circ$ and $4G^\circ$ for the rxn~~



and -1440 cal , respectively. Calculate the value of K_p at 500°C .

$$\underline{\underline{So \text{ I}^M}} \quad 4G^\circ = -RT \ln K_p$$

$$\Rightarrow K_p = e^{-\frac{4G^\circ}{RT}}$$

$$\therefore K_p_{25^\circ\text{C}} = e^{-\frac{1440}{1.987 \times 298}} = 1.3806$$

$$\text{Now, } \ln \frac{K_P 500^\circ\text{C}}{K_P 25^\circ\text{C}} = \frac{4H^\circ}{R} \cdot \frac{773 - 298}{773 \times 298}$$

$$\therefore K_p = 8.1647$$

Le-Châtelier's principle:-

Effect of temp, pressure, conc,
catalyst, inert gas.

Effect of Conc: - Bottles kept to normal



- ⑤ Increases concn of Fe^{3+} / CN^{\ominus} , shifted the eqd towards right.

reactant concn increases \rightarrow right direction
 product \rightarrow left direction.

Effect of pressure:-



- ④ increases in pressure shifted the 2O_3 towards right.

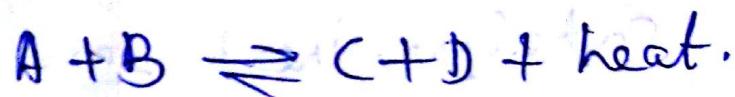


Increases in pressure shifted the eq'd forwards left.



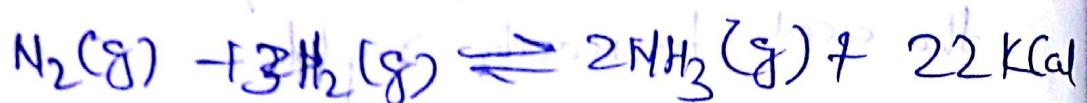
pressure has no effect.

Effect of temp:-



Increase of temp. shifted the eqth towards left.

Haber's process:-



- (a) Concⁿ of N₂ and H₂ should be high.
- (b) High pressure,
- (c) low temp.
- (d) Catalyst.

Contact process:-



- (a) Increase the Concⁿ of SO₂ and O₂.
- (b) High pressure
- (c) low temp.
- (d) Catalyst.



Burnt off and removed

Left off and removed

Left off and removed

Left off and removed

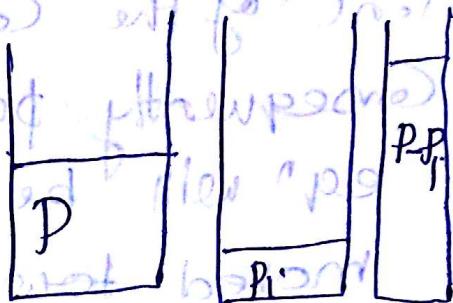
Effect of inert gas:-

① At Constant pressure:-

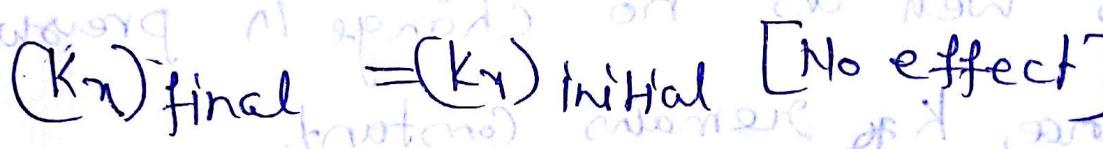
$$K_p = K_x \cdot (P)^{4n}$$

$$\therefore K_{p\phi} = K_x (\text{initial}) \cdot P^{4n}$$

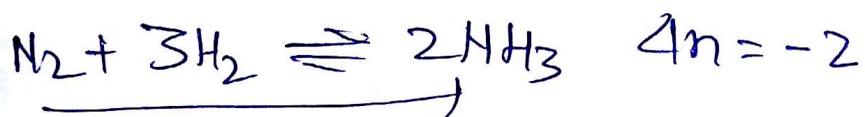
$$K_{p\phi} = K_x (\text{final}) \cdot (P - P_i)^{4n}$$



$$\frac{(K_x)_{\text{final}}}{(K_x)_{\text{initial}}} = \left(\frac{P}{P - P_i} \right)^{4n}$$



$$(K_x)_{\text{final}} = (K_x)_{\text{initial}} \quad [\text{No effect}]$$



$$(K_x)_{\text{final}} < (K_x)_{\text{initial}}$$

fowards left side



$$(K_x)_{\text{final}} > (K_x)_{\text{initial}}$$

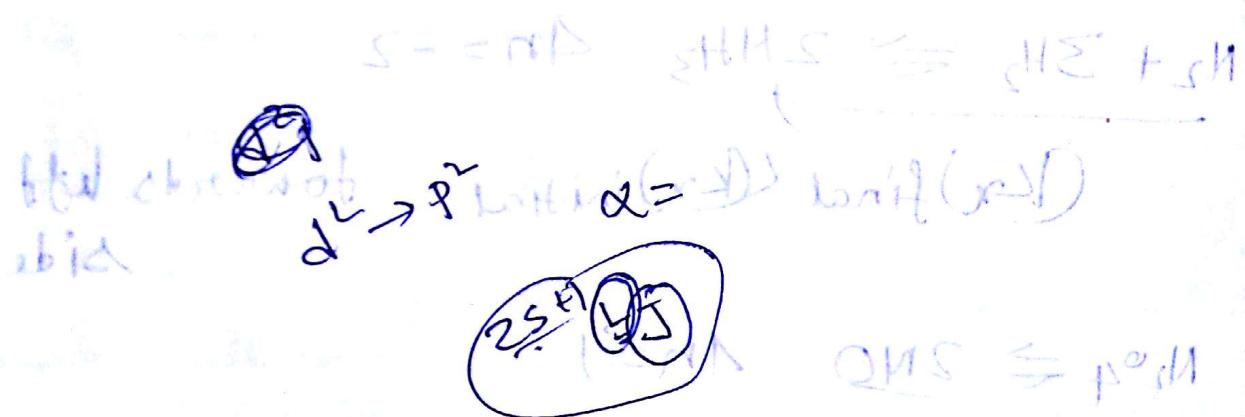
right direction

Explanation:-

At constant pressure, addition of solute increases the volume of the system. As a result, conc of the constituents decreases and consequently partial pressure decreases. Thus, eqn will be affected and it will be moved towards the side where conc is higher.

At conc Volume:-

No effect. No change in volume, so no change in p.t. pressure, as well as no change in pressure. Hence, K_p remains constant.



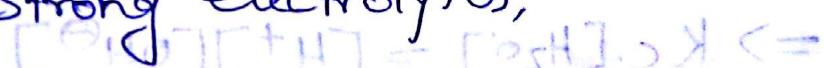
$$\text{If } P_A < P_B \Rightarrow Q_{\text{eq}} < 1$$

Tonic equilibrium:-



$\alpha = \text{degree of dissociation} = \frac{\text{total no. of ions produced}}{\text{total no. of original molecules}}$

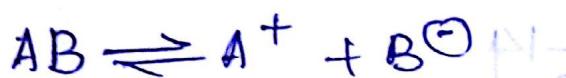
In case of strong electrolytes,



$$\alpha = 1 (100\%)$$

For weak electrolytes, $\alpha \ll 1$.

Ostwald's dilution law:- (specific to weak electrolytes)



Initially C $[C] = C_0$ $[C] = C_0 c^n$

At eqd. $C(1-\alpha) \propto \alpha$ $\alpha = \text{degree of dissociation}$

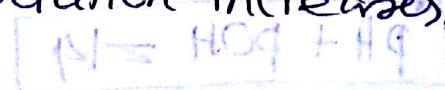
$$\therefore K_D = \frac{[A^+][B^-]}{[AB]} = \frac{\alpha C \cdot \alpha C}{C(1-\alpha)} = \frac{C\alpha^2}{C(1-\alpha)}$$

$$[\text{OH}^-]_{\text{tot}} = \text{OH}^- ; [\text{H}^+]_{\text{tot}} = \frac{C\alpha^2}{1}$$

Since $\alpha \ll 1$, $1 - \alpha \approx 1$

$$\therefore \alpha = \sqrt{\frac{K_D}{C}}$$

For weak electrolytes, as the concentration decreases, the degree of dissociation increases.



Ionic product of water:-



Initially C \rightarrow not possible to separate $= 0$

At equl. $C(1-\alpha) \approx \alpha$

$$\therefore K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

$$\Rightarrow K_c[H_2O] = [H^+][OH^-]$$

$$\Rightarrow K_w = [H^+][OH^-]$$

↓
It is constant at constant temp. and increases with increase of temp.

$$At 25^\circ C, K_w = 1 \times 10^{-14}$$

$$\Rightarrow [H^+][OH^-] = 10^{-14}$$

$$\Rightarrow [H^+] = [OH^-] = 10^{-7}$$

Concept of pH :-

$$pH = -\log [H^+]; pOH = -\log [OH^-]$$

$$pK_w = -\log [K_w]$$

for pure water, $[H^+] = 10^{-7} M \therefore pH = 7$

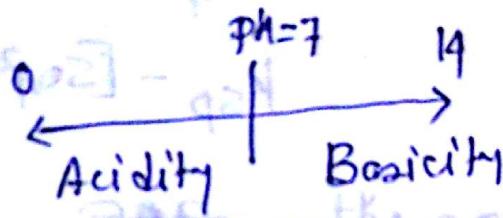
$$[OH^-] = 10^{-7} M; pOH = 7$$

$$pH + pOH = 14$$

$$pK_w = 14$$

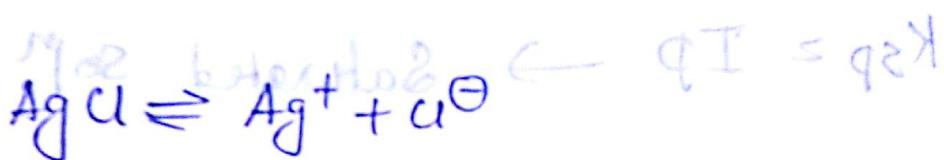
For strong acids, pH will be low

For bases, pH will be high.



Solubility product:-

When sparingly soluble salts like AgCl , Ag_2SO_4 , Ag_2CrO_4 , PbS , $\text{Al}_2(\text{SO}_4)_3$ are mixed with water, an equilibrium is established between the salts and their dissociated ions.



$$K_D = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]} \quad \text{(not normal)}$$

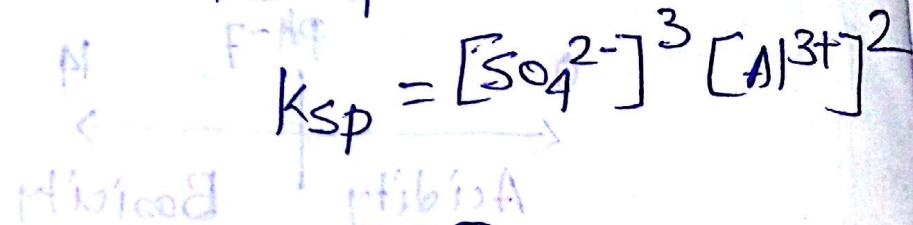
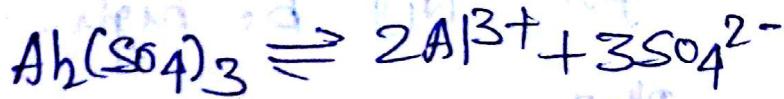
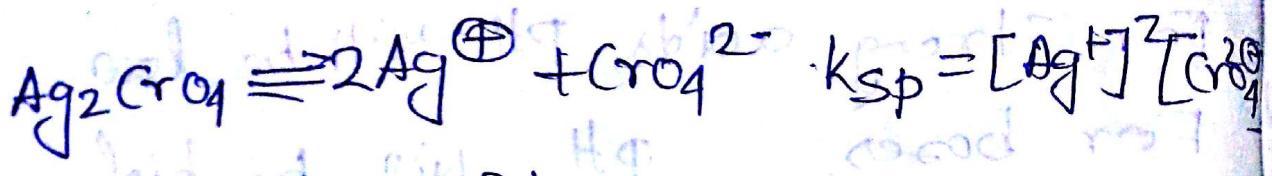
$$K_D \times [\text{AgCl}] = [\text{Ag}^+][\text{Cl}^-]$$

$$\Rightarrow K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$



Solubility product = product of the concentrations of constituents ions

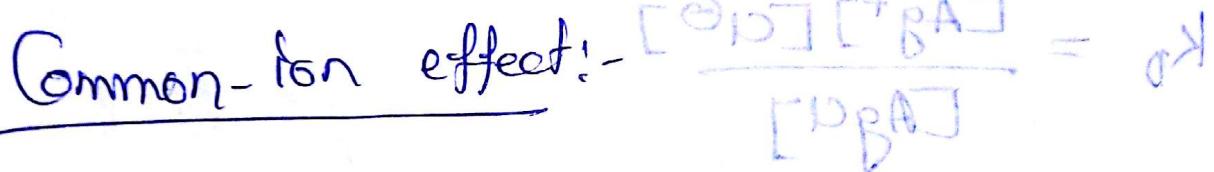
In a saturated solution of a sparingly soluble salt.



$K_{sp} > IP \rightarrow$ No precipitation

~~After mixing two un-saturated solns~~

$K_{sp} < IP \rightarrow$ Saturated precipitation occurs



$$[O]P[B]^{+}BA = [PBA] \times K$$

$$[O]P[B]^{+}BA = q \leq K$$

~~if to turborg = turborg gñidwz~~

~~no change in ion product conc~~

~~so no change in eqm~~

~~the eqm shifts~~

Reaction
Van't Hoff isotherm :- Variation of equilibrium constant with Temp.

$$\ln \frac{K_P_2}{K_P_1} = \frac{\Delta H^\circ}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\ln \frac{K_C_2}{K_C_1} = \frac{\Delta H^\circ}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

We know, $K_P = K_C (RT)^{4n}$

$$K_P = K_C (0.082 T)^{4n}$$

$$K_P = K_C \cdot (RT)^{4n}$$

$$K_P = K_C \cdot (P)^{4n}$$

Degeneration of Van't Hoff eqn:-

$$G = H - TS + \quad H = U + PV$$

$$dG = dH - TdS - SdT + PVdV + PdV + VdP = dG + VdP$$

$$= TdS + VdP - TdS - SdT = TdS + VdP$$

$$= VdP - SdT$$

$$dG_T = VdP \quad P = PV \quad \text{avioding p.s.t.A}$$

$$= \frac{nRT}{P} dP$$

$$\int_{G^\circ}^G dG_T = nRT \int_{P^\circ}^P dP$$

$$- RT \Delta P^\circ$$

$K^\circ = \frac{P}{G^\circ}$ \rightarrow refers standard state

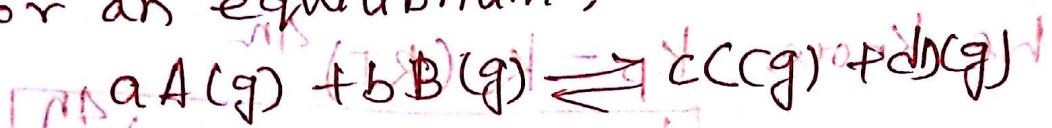
$$\Rightarrow G - G^\circ = nRT \ln \frac{P}{P_0}$$

$$\Rightarrow G - G^\circ = nRT \ln P$$

$$\Rightarrow G = G^\circ + nRT \ln P \quad \boxed{\text{Ansatz}} \quad \Rightarrow \bar{G} = \bar{G}^\circ + RT \ln P$$

Now, ~~G~~ \bar{G}

for an equilibrium,



$$\therefore \Delta G = \sum G_{\text{product}} - \sum G_{\text{reactant}}$$

$$= (\bar{G}_C^\circ + d\bar{G}_D^\circ) - (a\bar{G}_A + b\bar{G}_B^\circ)$$

$$= (\bar{G}_C^\circ + cRT \ln P_C + d\bar{G}_D^\circ + dRT \ln P_D)$$

$$- (a\bar{G}_A^\circ + aRT \ln P_A + b\bar{G}_B^\circ + bRT \ln P_B)$$

$$+ bRT \ln P_B)$$

$$fb + vb + ub = ab$$

$$qbv + pb = \frac{P_C \cdot P_D}{P_A^a \cdot P_B^b}$$

$$qv + pb = \frac{P_C \cdot P_D}{P_A^a \cdot P_B^b} - qb + 2bT =$$

$$\Delta G = \Delta G^\circ + RT \ln K_p$$

At equilibrium $\Delta G = 0$

$$\therefore \Delta G^\circ = -RT \ln K_p$$

$$K_p = e^{-RT/\Delta G^\circ}$$

but note $e^{-x} = \frac{1}{e^x}$

$$K_p = \frac{1}{e^{RT/\Delta G^\circ}}$$

$$qb \frac{T^a}{q^a} =$$

$$qb \left\{ \begin{array}{l} T^a = T^b \\ q^a = q^b \end{array} \right\}$$

Now, from Gibb's-Helmholtz eqn

$$\frac{d}{dT} \left(\frac{\Delta G^\circ}{T} \right) = -\frac{\Delta H^\circ}{T^2}$$

$$\Rightarrow \frac{d}{dT} \left[-\frac{RT \ln K_p}{T} \right] = -\frac{\Delta H^\circ}{RT^2}$$

$$\Rightarrow -R d \ln K_p = -\frac{\Delta H^\circ}{T^2} \cdot dT$$

$$\Rightarrow R' d \ln K_p = -\frac{\Delta H^\circ}{R} \cdot \frac{dT}{T^2}$$

$$\int_{K_p 1}^{K_p 2} d \ln K_p = \frac{\Delta H^\circ}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\boxed{\ln \frac{K_p 2}{K_p 1} = \frac{\Delta H^\circ}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]}$$

Similarly, $\boxed{\ln \frac{K_c 2}{K_c 1} = \frac{\Delta U^\circ}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]}$

The eq^l constant K_p for the rxn $\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g)$ is 2.95 at 400 K. Calculate the amount of PCl_5 formed when 1 mole of Cl_2 and 2 moles of PCl_3 are taken. Equilibrium pressure is 1 atm.

$$\Delta H^\circ = -419 \text{ J} + 865 \text{ cal/mol.}$$

Sol'n $K_p = 2.95$



At equilibrium $\Rightarrow x_{\text{PCl}_5} = \frac{x}{x+2-x+1-x}$

$$K_p = K_x \cdot (P)^{\frac{\Delta n}{\Delta f}} = \frac{x}{(1-x)(2-x)} \quad \text{eliminate}$$

$$x_{\text{Cl}_2} = \frac{1-x}{3-x}$$

$$x_{\text{PCl}_3} = \frac{2-x}{3-x}$$

$$K_p = \frac{x_{\text{PCl}_5}}{x_{\text{PCl}_3} \cdot x_{\text{Cl}_2}} = \frac{\frac{x}{3-x}}{\frac{(1-x)}{3-x} \times \frac{2-x}{3-x}} = \frac{x(3-x)}{(1-x)(2-x)}$$

$$= \frac{3x-x^2}{2-3x+x^2}$$

$x = ?$