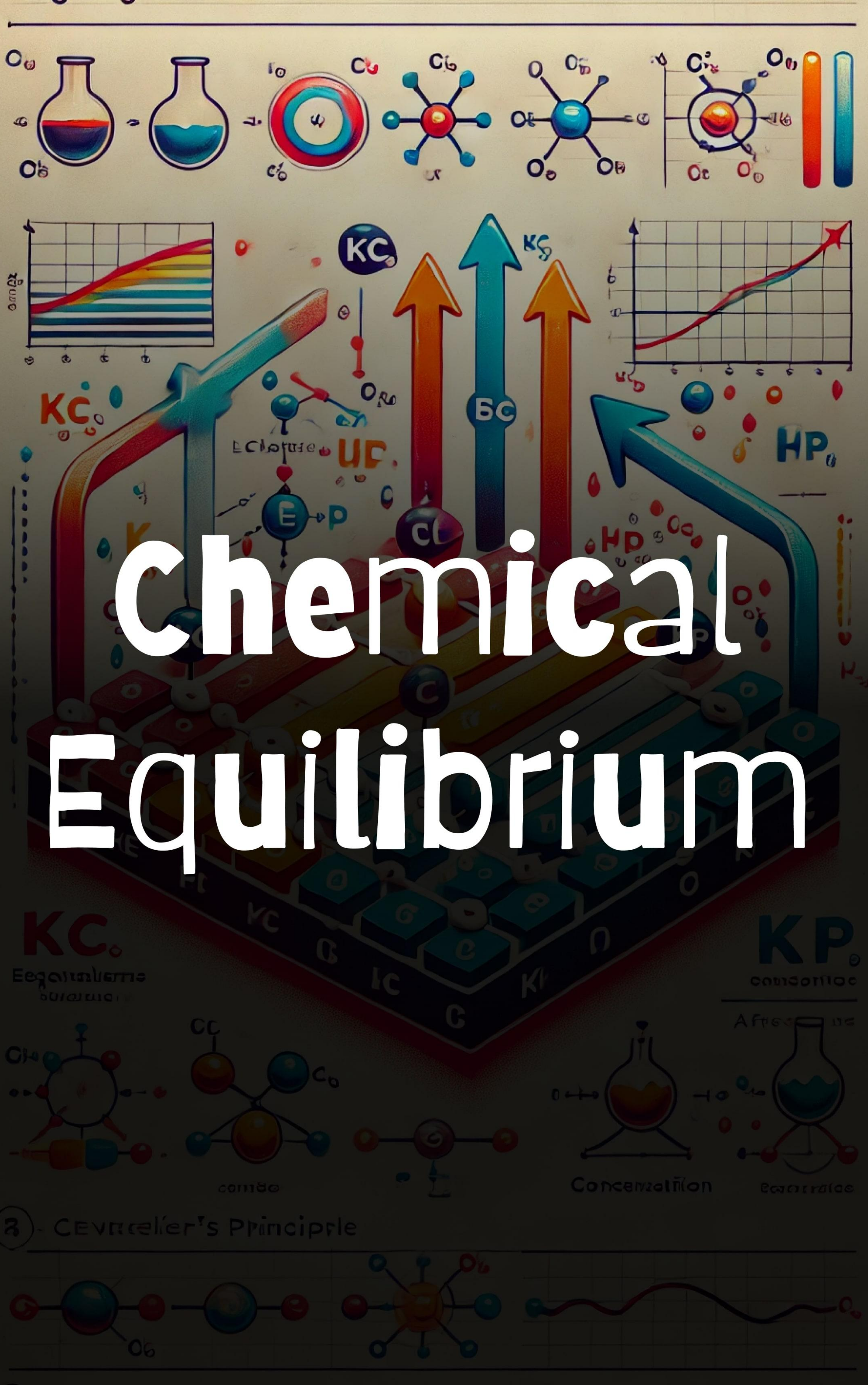
Chemical Equilibrium



CHEMICAL EQUILIBRIUM

Reversible and unreversible reaction – Reaction can be classified into two types.

1. IRREVERSIBLE REACTION

The reactions in which the reactants are converted into products and products are not converted into the reactants again are called as *irreversible reactions*. These reactions are denoted by '⟶'.

An irreversible reaction always tends towards completion.

The following types of reactions are generally irreversible:–

1. THERMAL DECOMPOSITION

Decomposition of a substance in an open vessel is irreversible.

e.g:–

i $CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow$

ii $2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2\uparrow$

2. NEUTRALIZATION REACTION

Neutralization reaction between a strong acid and strong base is irreversible.

eg:- (i) $HCL + NaOH \longrightarrow NaCl + H_2O$

(ii) $H_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + H_2O$

3. PRECIPITATION REACTION

The Reaction between two electrolytes to form a precipitate is generally irreversible.

eg:- (i) $AgNO_3 + KCL \longrightarrow AgCl\downarrow + KNO_3$

4. COMBUSTION REACTION

Combustion of an organic substance is generally irreversible.

② REVERSIBLE REACTION

The reaction in which reaction form products and products are again converted into reactants are called as reversible reaction

These reaction are denoted by a 'double headed arrow.'

$A \rightleftharpoons B$

The following types of reaction are general reversible :-

1. THERMAL DECOMPOSITION IN A CLOSED VESSEL

eg :- $CaCO_3 \rightleftharpoons CaO + CO_2$

$2KClO_3 \rightleftharpoons 2KCl + 3O_2$

2. NEUTRALIZATION REACTION

The reaction in which either acid or base or both are weak are reversible.

eg :- i $\underset{(WA)}{CH_3COOH} + \underset{(SB)}{NaOH} \rightleftharpoons CH_3COONa + H_2O$

ii $\underset{(SA)}{HCL} + \underset{(WB)}{NH_4OH} \longrightarrow NH_4CL + H_2O$

iii $CH_3COOH + NH_4OH \rightleftharpoons CH_3COONH_4 + H_2O$

3. HYDROLYSIS REACTION

The hydrolysis reaction of salts of :-

Weak Base + Strong Acid

WA + SB

WA + WB

are reversible.

- Reversible reactions never tends to completion.

CONCEPT OF EQUILIBRIUM STATE

The state attained by a system in which the system has no tendanc for a change untill an external stimulation is given on the basis of behaviour of equilibrium state, it is classified into three types :-

I. MECHANICAL EQUILIBRIUM

a. Static Mechanical equilibrium

The Position or speed of a system with time, then it is called as mechanical equilibrium.

If the position of the system doesn't change with time, it is called static mechanical equilibrium.

CHARACTERISTICS OF CHEMICAL EQ^n

i It can be obtained from either side of the reaction.

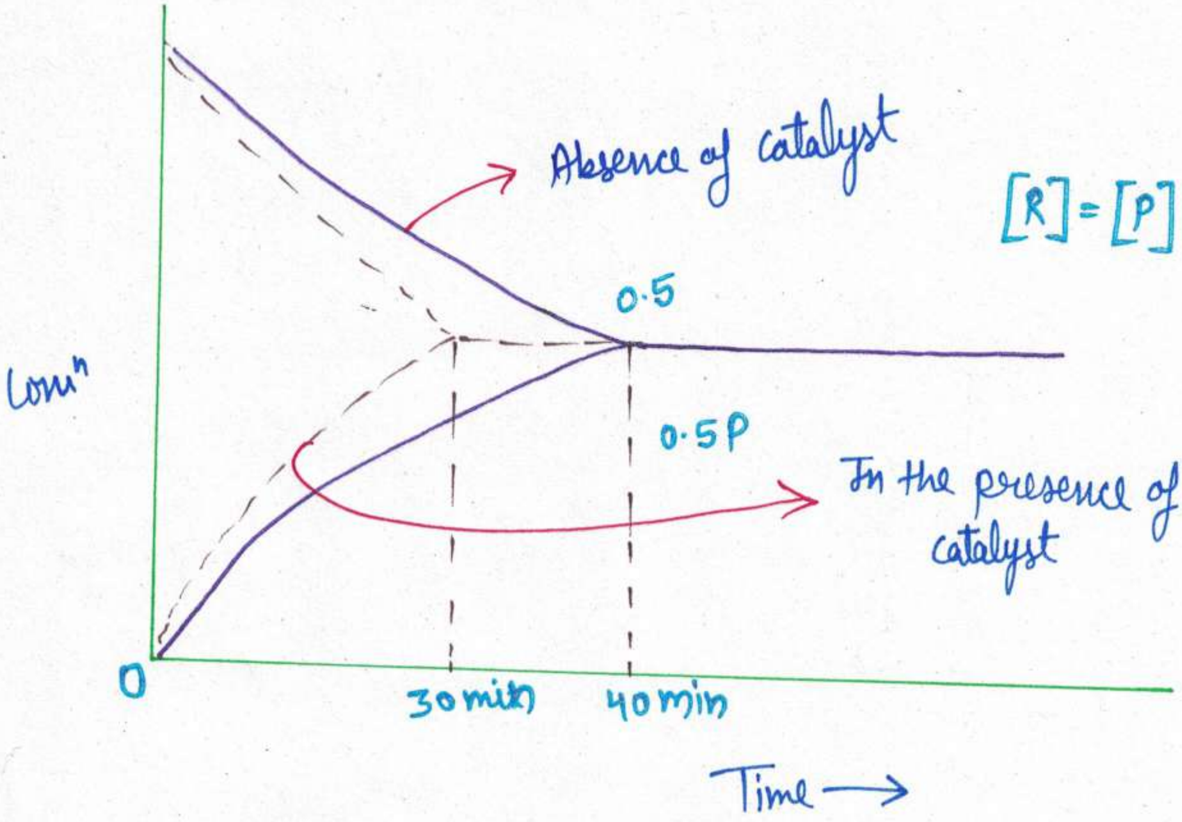
eq:- @ $2SO_3 \rightleftharpoons 2SO_2 + O_2$

$2SO_2 + O_2 \rightleftharpoons SO_3$

ii Chemical equation is "dynamic" in nature, i.e:- the reaction takes place in both the directions with the same rate but it never stops.

iii At eq^n, all measurable properties of system such as surface tension, viscocity, refraction index (μ), concentration, temperature pressure etc. donot change with time.

IV A catalyst doesn't effect the eq^n state but in presence of a catalyst eq^m is achieved quickly as it increases weight of both forward and backward reaction to the same extent.



LAW OF MASS ACTION

The rate of an elementary reaction (single-step) is directly proportional to product of active masses of reactants raised to a power equal to stichiometric co-efficient in a balanced chemical equation.

$$m_1A + m_2B \rightleftharpoons n_1C \quad n_2D$$

$$\boxed{r = a_A^{m_1} \cdot a_B^{m_2}}$$

In a solution phase reaction

$$a_A \propto \text{Molarity} \Rightarrow a_A = \gamma[A]$$

$$a_A \propto \text{Mole fraction} \Rightarrow a_A = \gamma X_A$$

{Where γ and γ are constents & eq. to 1 for dil. solⁿ}

For detail solⁿ

$$a_A = [M] \quad \text{or} \quad a_A = X_A$$

For gas phase reaction

$$a_A \propto P_A \Rightarrow a_A = f \cdot P_A$$

{Where F=1}

$$\boxed{a_A = P_A}$$

$a_{solids} = 1$

$a_{pure\ liquid} = 1$

$$m_1A + m_2B \rightleftharpoons n_1C + n_2D$$

Apply Law of Mass Action

$$r_F \propto [A]^{m_1} \cdot [B]^{m_2}$$

$$r_F = k_F [A]^{m_1} \cdot [B]^{m_2}$$

↓

Rate const. of forward reaction

$$r_b \propto [C]^{n_1} \cdot [D]^{n_2}$$

$$r_b = k_b [C]^{n_1} \cdot [D]^{n_2}$$

↓

Rate Const. of backward reaction

[ ] → Constant

At Equilibrium

$$r_F = r_b$$

$$k_F \cdot [A]_{eq}^{m_1} \cdot [B]_{eq.}^{m_2} = k_b [C]_{eq}^{n_1} \cdot [D]_{eq.}^{n_2}$$

$$K_c = \frac{k_F}{k_b} = \frac{[C]_{eq}^{n_1} \cdot [D]_{eq}^{n_2}}{[A]_{eq}^{m_1} \cdot [B]_{eq.}^{m_2}}$$

↓

equilibrium constant

Write K_c constants for the foll reaction :-

i $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

ii $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

iii $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)} \uparrow$

Ans. i $K_c = \frac{[NH_3]^2}{[H_2]^3 . [N_2]^1} = \frac{[mol/L]^2}{[mol/L]^4} = [mol/L]^{-2}$

ii $K_c = \frac{[SO_3]^2}{[SO_2]^2 . [O_2]^1} = [mol/L]^{-1}$

iii $K_c = \frac{[CaO]_s^1 \, [CO_2]^1}{[CaCO_3]_s} = \frac{[1][CO_2]^1}{[1]} = [CO_2]^1 = [mol/L]^1$

iv $2KCL_{3(s)} \overset{\Delta}{\rightleftharpoons} 2KCL_{(s)} + 3O_2(g)$

$K_c = \frac{[O_2]^3 \cdot 1}{1} = [O_2]^3$

$m_1A + m_2B \rightleftharpoons n_1C + n_2D$

$$K_c = \frac{[C]^{n_1} . [D]^{n_2}}{[A]^{m_1} . [B]^{m_2}} = \frac{[mole/L]^{n_1} . [mole/L]^{n_2}}{[mole/L]^{m_1} . [mole/L]^{m_2}} = \frac{[mole/L]^{n_1+n_2}}{[mole/L]^{m_1+m_2}}$$

units of $K_c = [mole/L]^{(n_1+n_2)-(m_1+m_2)}$

EQUILIBRIUM CONSTANT IN TERMS OF PRESSURE

- Liquids, solids are not taken into consideration

$$m_1 \underset{(g)}{A} + m_2 \underset{(g)}{B} \rightleftharpoons n_1 \underset{(g)}{C} + n_2 \underset{(g)}{D}$$

$$\boxed{K_p = \frac{P_C^{n_1} \cdot P_D^{n_2}}{P_A^{m_1} \cdot P_B^{m_2}}} = \frac{K_f}{K_b}$$

K_p → equilibrium constant (Pressure)

P_C, P_D, P_A, P_B are Partial pressures

units of K_p

$$\boxed{K_p = (atm)^{(n_1+n_2)-(m_1+m_2)}}$$

(m_1+m_2) → No. of moles of gasous reactants

(n_1+n_2) → No. of moles of gaseous products

QUE:- Write kp constants for the following reaction:-

i. $PCl_{5}(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

ii. $CaCO_3(g) \rightleftharpoons CaO_{(s)} + CO_2(g)$

iii. $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

Ans:-

i. $$K_p = \frac{(P_{PCl_3})^1 \cdot (P_{Cl_2})^1}{(P_{PCl_5})^1} = (atm)$$

ii $$K_p = \frac{(P_{CO_2})^1}{(P_{CaCO_3})^1} = [M^0L^0T^0]$$

iii $$K_p = \frac{(P_{H_2})^1(P_{I_2})^1}{(P_{HI})^2} = [M^0L^0T^0]$$

iv $$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_p = \frac{(P_{NH_3})^2}{(P_{H_2})^3 \cdot (P_{N_2})^1} = (atm)^{-2}$$

Relationship Between K_p & K_c

$$\underset{(g)}{aA} + \underset{(g)}{bB} \rightleftharpoons \underset{(g)}{cC} + \underset{(g)}{dD}$$

$$K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \text{ ——— } ①$$

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right) \cdot RT = C_M RT$$

eq ① becomes

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

$$k_p = \frac{[C]^c \cdot [D]^d \cdot (RT)^{(c+d)-(a+b)}}{[A]^a \cdot [B]^b}$$

$$\boxed{K_p = K_c\,(RT)^{\Delta n}}$$

$\Delta n = (c+d) - (a+b)$

Write the relation between k_p and k_c :-

i $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

ii $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$

iii $CaCO_{3(s)} \overset{\Delta}{\rightleftharpoons} CaO_{(s)} + CO_{2(g)}$

iv $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$

i $k_p = K_c\,(RT)^{\Delta n}$

$K_c\,(RT)^{(2)-(4)}$

$$\frac{[NH_3]^1}{[H_2]^3[N_2]^1} \cdot (RT)^{-2} = \underline{K_c\,(RT)^{-2}}$$

If $T = 273\ K$

$K_p = \frac{K_c}{(22.4)^2} ; K_c 7 k$

ii $$k_p = \frac{[SO_2]^2 \cdot [O_2]^1}{[SO_3]^2} \cdot (RT)^1 = \underline{(K_c)(RT)}$$

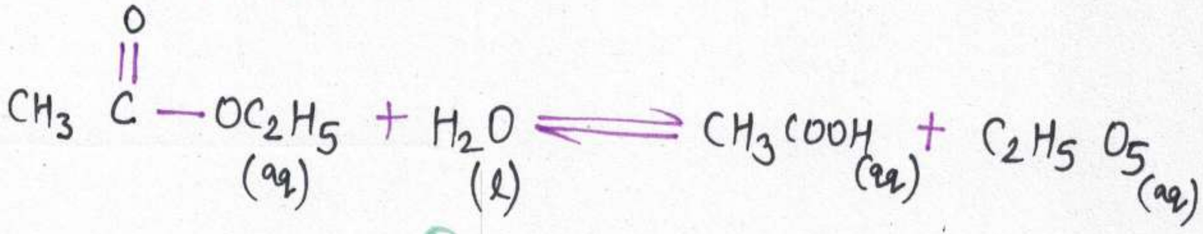
iii $k_p = [CO_2]^{+} \cdot [RT]^1 = \underline{K_c\,(RT)}$

iv

$$K_p = \frac{[H_2]^1\,[I_2]^1}{[HI]^2}\cdot(RT)^0$$

$$= \frac{[H_2]\,[I_2]^1}{[HI]^2}\cdot 1 = \underline{(K_c)}$$

V



$$CH_3\overset{\overset{O}{\|}}{C}-OC_2H_5{}_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + C_2H_5O_5{}_{(aq)}$$

$$K_p = K_c(RT)^{2-2}$$

$$K_p = K_c$$

Not defined

But all are liquids

$$\therefore\ K_p = K_c = 0$$

K_p is not defined as none of the reactants and products are gaseous.

CHARACTERISTICS OF EQUILIBRIUM CONSTANT

Equilibrium constant of a reaction depends only on "temperature". The temparature remains constant the equilibrium constant also remains same.

Equilibrium constant doesn't depend on initial concentration of reactants and products.

Presence of an inert material doesn't change the equilibrium constant.

Presence of a material which reacts with either reactants or products changes the equation constant.

Presence of a catalyst doesn't change the equilibrium constant but in the presence of a catalyst the equilibrium is establishe quickly.

For the reactions, "K >>>> 1", equilibrium almost lies towards products and equilibrium concⁿ of products are very high as compared to eqᵐ concentration of the reactants.

For the reactions, "K <<<< 1", the equilibrium lies towards the reactants and the equilibrium concⁿ of reactants is very high as compared to products.

FACTORS AFFECTING EQUILIBRIUM CONSTANT

Mode of writing the reaction

$A_2 + B_2 \rightleftharpoons 2AB$

$$K_c = \frac{[AB]^2}{[A_2].[B_2]}$$

$2AB \rightleftharpoons A_2 + B_2$

$$K_c' = \frac{[A_2][B_2]}{[AB]^2}$$

$$\therefore K_c' = \frac{1}{K_c}$$

If the reaction is reversed, the eq^{m} constant of the reversed reaction is equal to the reciprocal of the initial reaction.

ii Stichiometric co-efficients of the equilibrium reactions.

$$A_2 + B_2 \rightleftharpoons 2AB$$

$$K_c = \frac{[AB]^2}{[A_2].[B_2]}$$

Multiplying the eq^{m} with 2

$$2A_2 + 2B_2 \rightleftharpoons 4AB$$

$$K_c' = \frac{[AB]^4}{[A_2]^2.[B_2]^2}$$

$$K_c' = \left\{\frac{[AB]^2}{[A_2].[B_2]}\right\}^2$$

$$\therefore K_c' = K_c^2$$

If the reaction is multiplied with some no. then the equilibrium constant of the new reaction is equal to the eq^{m} constant of the initial reaction raised to a power of the number.

	Reaction (K_c)	K_c'
×	3	K_c^3
×	4	K_c^4
×	n	K_c^n

iii

Temperature

The only experimental factor that has an effect on the equilibrium constant is temperature. It can be explained by using "Vant Hoff's equation".

$$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{2.303R} \cdot \left[\frac{1}{T^1} - \frac{1}{T^2}\right]$$

K_2 is eq^m const. at temp. T_2.

K_1 is eq^m const. at temp. T_1.

$\Delta H \rightarrow$ Enthalpy of the reaction.

- ΔH is -ve ⟶ exothermic
- ΔH is +ve ⟶ endothermic
- ΔH is 0 ⟶ Thermo neutral

If $\Delta H = 0$;

$$\log\left(\frac{K_2}{K_1}\right) = 0$$

$$\therefore \boxed{K_2 = K_1}$$

Equilibrium constant of thermoneutral reaction doesn't depend on temperature.

If $\Delta H = -ve$;

$T_2 > T_1$

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{T_2 - T_1}{T_1 \cdot T_2}$$ is a +ve quantity

$\therefore$ ΔH is −ve ;

$$\log\left(\frac{K_2}{K_1}\right) < 0$$

$$\therefore \boxed{K_2 < K_1}$$

equilibrium constant of exothermic reaction decreases with the ↑ in temperature.

- If $\Delta H = +ve$;

$T_2 > T_1$

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{T_2 - T_1}{T_1 T_2}$$ is +ve

$\therefore$ ΔH is +ve

$$\log\left(\frac{K_2}{K_1}\right) > 0$$

$$\therefore \boxed{K_2 > K_1}$$

equilibrium constant of endothermic reaction ↑ with ↑ in temperature

Equilibrium Constant of combined equilibrium reaction :-

$A \rightleftharpoons B$ $\quad K_1 = \frac{[B]}{[A]}$

$B \rightleftharpoons C$ $\quad K_2 = \frac{[C]}{[B]}$

$C \rightleftharpoons D$ $\quad K_3 = \frac{[D]}{[C]}$

$A \rightleftharpoons D \Rightarrow ?$

$\therefore$ on adding the eq^n;

$$A + \cancel{B} + \cancel{C} \rightleftharpoons \cancel{B} + \cancel{C} + D \Rightarrow A \rightleftharpoons D$$

$$\therefore\ K_4 = \frac{[D]}{[A]}$$

$$\frac{[D]}{\cancel{[C]}} \cdot \frac{\cancel{[C]}}{\cancel{[B]}} \cdot \frac{\cancel{[B]}}{[A]}$$

$2NO + O_2 \rightleftharpoons 2NO_2 \longrightarrow K_1$

$2NO + Br_2 \rightleftharpoons 2NO_2Br \longrightarrow K_2$

If the equation are added, then the eqⁿ constants are multiplied.

Q. Calculate equilibrium constant of :-

(i) $2NO + O_2 \rightleftharpoons 2NO_2 \longrightarrow K_1$

$2NO + Br_2 \rightleftharpoons 2NO_2Br \longrightarrow K_2$ ②

$NO_2Br \rightleftharpoons \frac{1}{2}Br + \frac{1}{2}O_2 + NO \longrightarrow K_3 = ?$

A. (i) $$K_1 = \frac{[NO_2]^2}{[NO]^2\,[O_2]^1}$$

$$K_2 = \frac{[NO_2][Br]^2}{[NO_2]^2\,[Br_2]^1}$$

$$K_3 = K_1 \cdot K_2 = \frac{[NO_2]^2}{[NO]^2 \cdot [O_2]^1} \cdot \frac{[NO_2Br]^2}{[NO_2]^2\,[Br_2]}$$

As we have multiplied by ½

$$K_3 = \left(\frac{1}{K_1 \cdot K_2}\right)^{1/2} = \left\{\frac{[Br_2]\cdot[O_2].[NO]^2}{[NO_2]\,[Br]^2}\right\}^{1/2}$$

(as we have reversed the reaction)

After adding ① & ②;

$$Br_2 + 2NO + O_2 \rightleftharpoons 2NO_2Br$$

$$2NO_2Br \rightleftharpoons Br_2 + O_2 + 2NO$$

$$NO_2Br \rightleftharpoons \tfrac{1}{2}Br_2 + \tfrac{1}{2}O_2 + NO$$

ii $CoO_{(s)} + H_{2(g)} \rightleftharpoons Co(s) + H_2O_{(g)}$

$\hookrightarrow K_c = 67$

$CoO_{(s)} + CO_{(g)} \rightleftharpoons Co(s) + CO_2$

$\hookrightarrow K_c = 490$

Calculate:- K_c of $\rightarrow$

$CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$

A. ii $CoO_{(s)} + H_{2(g)} \rightleftharpoons Co_{(s)} + H_2O_{(g)}$

$\hookrightarrow 67$

$CoO_{(s)} + CO_{(g)} \rightleftharpoons Co_{(s)} + CO_{2(g)}$

$\hookrightarrow 490$

We need to cancel $Co_{(s)}$

Therefore, reverse the reaction ②;

$$CoO_{(g)} + H_{2(g)} \rightleftharpoons \cancel{Co_{(s)}} + H_2O_{(g)}$$

$\hookrightarrow 67$

$$\cancel{Co_{(s)}} + CO_{2(g)} \rightleftharpoons CoO_{(s)} + CO_{(g)}$$

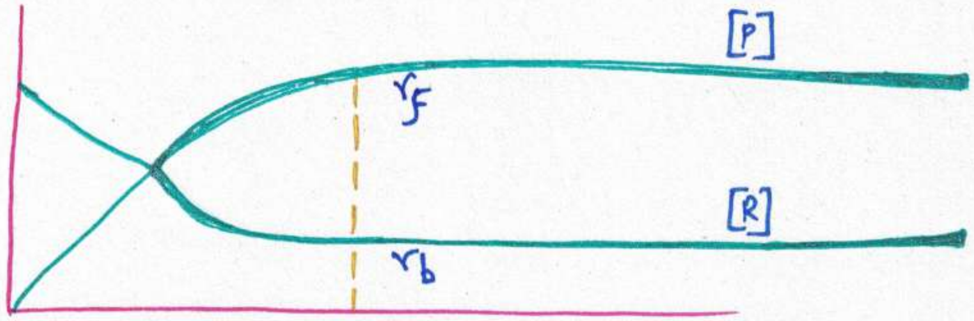
$\hookrightarrow 1/490$

$$\cancel{CoO_{(g)}} + H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + \cancel{CoO_{(s)}} + CO_{(g)}$$

$$\therefore K_c = \frac{67}{490}$$

Write if the following graphs show equilibrium state and whether [R] = [P] ?

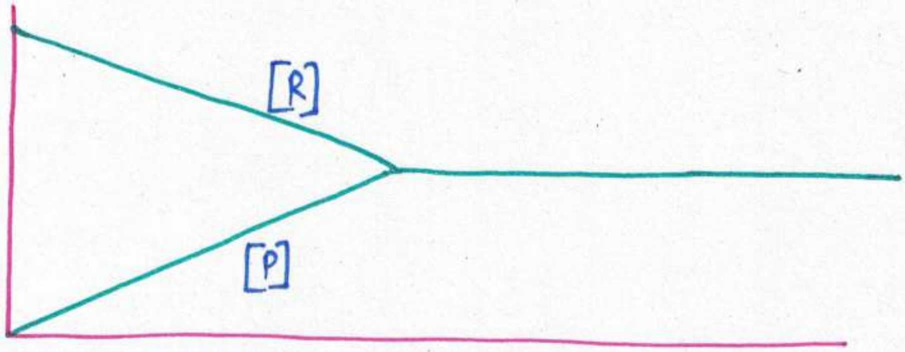
i



[R] = [P]

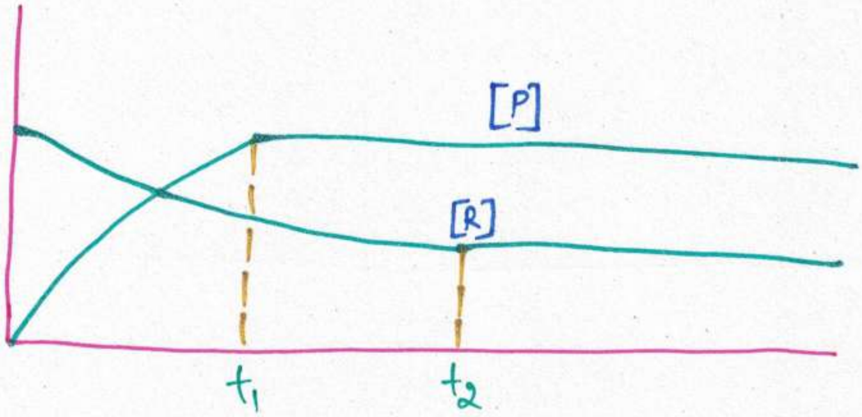
No equilibrium, no. overlapping of the rates

ii



equilibrium is there, Conc^n is also same

iii



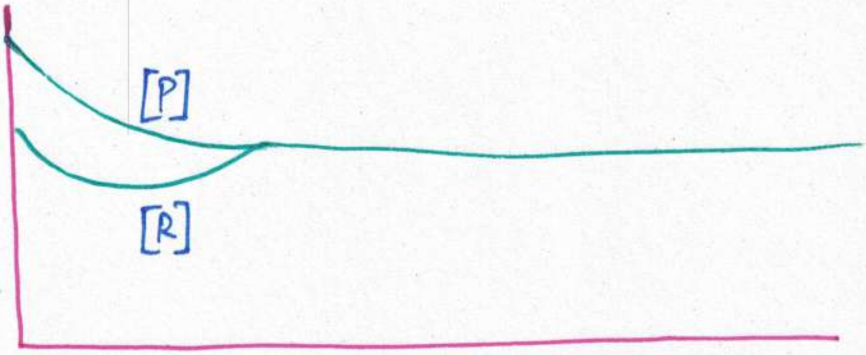
No equilibrium (time is different), Conc^n not same.

iv

Both the rates have been at eq^m from the beginning.

Conc^n is same.

V



No eq^m (Both rates can't be decreasing) $conc^n$ not same.

K_c and K_p are temperature dependent.

$A + B \rightleftharpoons C + D$ If initially A and B are in the ratio 2:1 at equilibrium $conc^n$ of [B] and [D] are same? Calculate K_p & K_c?

Ans:- a. $A + B \rightleftharpoons C + D$

	A	B	C	D
$t=0$	$2a$	a		
$t=t$	$2a-x$	$a-x$	x	x

$$[B] = [D]$$

$$\frac{a-x}{V} = \frac{x}{V}$$

$$\therefore \boxed{x = \frac{a}{2}}$$

$$K_c = \frac{[C].\cancel{[D]}}{\cancel{[B]}.[A]} = \left[\frac{a}{2V}\right] \Big/ \left[\frac{2a - a/2}{V}\right]$$

$$= \left[\frac{a}{2}\right] \Big/ \left[\frac{3a}{2}\right]$$

$$\boxed{K_c = 1/3} = K_p$$

b. $A + B \rightleftharpoons C + D$ Ratio = 2:1 for A and B. At eq^m conc^n of B = Conc^n of D. find $K_c = ?$

Ans:- $A + 2B \rightleftharpoons C + D$

$t=0$ $(2a)$ (a)

$t=t$ $(2a-x)(a-2x)$ x x

$$[B] = [D]$$

$$\frac{a-2x}{\cancel{V}} = \frac{x}{\cancel{V}}$$

$$\boxed{x = \frac{a}{3}}$$

$$K_c = \frac{[C][D]}{[A].[B].[B]} . V$$

$$= \frac{[a/3] . V}{\left[2a - \frac{a}{3}\right] . \left[a - \frac{2a}{3}\right]}$$

$$\boxed{K_c = \frac{3V}{5a}}$$

c. $A + 2B \rightleftharpoons 2C + D$

Ratio = 2:1, $[B] = [D]$

Ans:- $A + 2B \rightleftharpoons 2C + D$

$t=0$ $2a$ a

$t=t$ $2a-x$ $a-2x$ $2x$ x

$$\Rightarrow [B] = [D]$$

$$a - 2x = x$$

$$\boxed{x = \frac{a}{3}}$$

$$\Rightarrow \frac{\left[\frac{2a}{3}\right]^2 \cdot \left[\frac{a}{3}\right]}{\left[2a - \frac{a}{3}\right]\left[a - \frac{2a}{3}\right]^2}$$

$$\Rightarrow 4/5$$

DEGREE OF DISASSOCIATION

This is the disassociation out of one mole.

$$A_n \rightleftharpoons nA$$

A_n	nA
a	
$a - x$	nx
$a - a\alpha$	$na\alpha$

$a \longrightarrow x$

$1 \longrightarrow x/a$

$\alpha = x/a \Rightarrow x = a\alpha$

$$2A \rightleftharpoons B + C$$

a

$a-2x$

$$a \longrightarrow 2x$$

$$1 \longrightarrow 2x/a$$

$$\alpha = \frac{2x}{a} \Rightarrow x = \frac{a\alpha}{2}$$

$$a - a\alpha \longrightarrow n\left(\frac{a\alpha}{2}\right) + n\left(\frac{a\alpha}{2}\right)$$

$(a(1-\alpha))$

?

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

If $\alpha = 0.3$ equilibrium pressure is 20atm ; what is the value of $K_p = ?$

A.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

	PCl_5	PCl_3	Cl_2
$t=0$	1	0	0
$t=1$	0.7	0.3	0.3

$$K_p = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$\frac{\left(\frac{0.3}{1.3} \times 20\right) \cdot \left(\frac{0.3}{\cancel{1.3}} \times \cancel{20}\right)}{\left(\frac{0.7}{\cancel{1.3}} \times \cancel{20}\right)}$$

$$\boxed{K_p = \frac{180}{91} \text{ atm}}$$

SHORTCUT

If α is provided we want to calculate K_p for the reaction, we will assume initial mole as unity.

If α is very small compared to unity, we can take;

$$(1-\alpha) \approx 1$$
$$(1+\alpha) \approx 1$$

If α is less than "0.07" then we consider it to be very small as compared to unity.

What will be K_p if degree of disassociation is small as compared to unity? T_P at eq^m = P.

Ans:-

$$A_3B_2 \rightleftharpoons 3A + 2B$$

$$K_p = \frac{[A]^3 . [B]^2}{[A_3B_2]^1}$$

$\alpha = 1$

$$A_3B_2 \rightleftharpoons 3A + 2B$$

t=0   1   0   0

t=t $(1-\alpha)$ (3α) (2α)

$(1-\alpha \simeq 1)$

$$K_p = \frac{[A]^3[B]^2}{[A_3B_2]^1} \Rightarrow \frac{\left(\frac{3\alpha}{1+4\alpha}\cdot P\right)^3 \left(\frac{2\alpha}{1+4\alpha}\cdot P\right)^2}{\left(\frac{1-\alpha}{1+4\alpha}\cdot P\right)}$$

$$= \frac{27\alpha^3 P^3 \times 4\alpha^2 P^2}{P} \quad \{1-\alpha = 1\}$$

$$= 108\,\alpha^5 P_T^4$$

$$AB_{2(g)} \rightleftharpoons A_{(g)} + 2B_{(g)}$$

For the equilibrium Kp and total pressure P is given. If α is small as compared to unity, find α in terms of Kp and P?

Ans:-

	AB_2	$\rightleftharpoons$	A	$+$	$2B$
$t=0$	1		0		0
$t=t$	$(1-\alpha)$		α		2α

$$K_p = \frac{[A].[B]^2}{[AB]'} = \frac{\left(\frac{\alpha}{1+\alpha}\cdot P\right).\left(\frac{2\alpha}{1+\alpha}\cdot P\right)^2}{\left(\frac{1-\alpha}{1+\alpha}\cdot P\right)}$$

$1-\alpha \approx 1 \qquad 1+\alpha \approx 1$

$$\therefore \; K_p = 4\alpha^3 P^2$$

$$\boxed{\alpha = \left(\frac{K_p}{4P^2}\right)^{1/3}}$$

VAPOUR DENSITY CALCULATION FROM DEGREE OF DISSOCIATION

$$A_n \rightleftharpoons nA$$

$t=0 \quad a \qquad\qquad 0$

$t=t \quad a(1-\alpha) \qquad n a\alpha$

{ Total moles $= a(1-\alpha) + n a \alpha$

By mass conservation ;

$$a \cdot M_{A_n} = a\left[1+(n-1)\alpha\right] M_{mix}$$

$$VD_{mix} = \frac{M_{mix}}{2}$$

$$M_{mix} = 2 \cdot VD_{mix}$$

SHORTCUT :- Take "a" as 1 because "a" will be cancelled out both sides.

?

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

If $\alpha = 0.5$, then calculate the V.D of the mixture.

Ans:- $$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_2$$

$t=0 \quad 1 \qquad 0 \qquad 0$

$t=1 \quad 0.5 \qquad 0.5 \qquad 0.5$

Moles in total $= 1.5$

$$1 \cdot (208.5) = 1 \cdot (1.5) \cdot (VD_{mix}) \cdot 2$$

$$\boxed{VD_{mix} = \frac{208.5}{3} = 69.5g}$$

$N_2O_4 \rightleftharpoons 2NO_2$, at 27°C, If the degree of dissociatio
is 0.2 calculate :-

1. K_p and K_c
2. V.D of mixture
3. what will be value of total pressure at equilibrium, if the volume is 2L ?

Ans:- $N_2O_4 \rightleftharpoons 2NO_2$

$t=0 \quad 1 \rightleftharpoons 0$

$t=0 \quad 0.8 \rightleftharpoons 0.4$

$(1-\alpha) \qquad (2\alpha)$

$t = 300K$

1. Total moles $= 1.2$

$(a)(92) = a[1.2].(VD_{mix}).2$

$(92) = (VD)\ 2.4$

$(VD) = \frac{\cancel{920}^{\cancel{230}\ 115}}{\cancel{24}_{\cancel{6}\ 3}} = \frac{115}{3} = 38.3$

2. $K_p = \frac{(NO_2)^2}{(N_2O_4)^1} = \frac{(P_{NO_2})^2}{(P_{N_2O_4})^1}$

$$= \frac{\left(\frac{2\alpha}{1+\alpha} \cdot P_T\right)^2}{\left(\frac{1-\alpha}{1+\alpha}\ P_T\right)}$$

$$K_p = \frac{4\alpha^2}{(1-\alpha)^2} \cdot P_T$$

$PV = nRT$

$P_T \cdot 2 = (1+\alpha)\cdot\frac{1}{\cancel{12}}\cdot\overset{25}{\cancel{300}}$

$$\boxed{P_T = \frac{25(1+\alpha)}{2}}$$

$= \frac{25\times\overset{0.6}{\cancel{1.2}}}{\cancel{2}} = 15$ atm

$\Delta n = 1$

$\therefore K_p = \frac{\cancel{4\times0.4}\times 15}{\cancel{0.64}\;\;4} = \frac{15}{4}$

$\frac{15}{4} = K_c\left(\frac{1}{12}\cdot\frac{\cancel{300}}{\cancel{25}_5}\right)$

$$\boxed{K_c = \frac{3}{20}}$$

$$\boxed{K_p = \frac{15}{4}}$$

3. $P_T = 15$ atm

SIGNIFICANCE OF REACTION QUOTIENT

$$aA + bB \longrightarrow cC + dD$$

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

It is at general time "t"

i If $Q_c = K_c \longrightarrow$ Equilibrium

ii If $Q_c > K_c \longrightarrow$ Backward direction iii If $Q_c < K_c$ ⟶ Forward direction

At any time of equilibrium $A + B \rightleftharpoons C + D$, each reactant and product were 2 moles. In which direction, will the eq^m move. if:-

i $K_c = 4$ ii 1 iii $K_c = 0.25$

Ans:- ii equilibrium

i $Q_c = \frac{[C]^2[D]^2}{[A]^2[B]^2} = 1$

$K_c = 4$ <u>Forward</u>

$Q_c < K_c$

iii $Q_c = 1$ $K_c = 0.5$ <u>Backward</u>

What will be equilibrium con^n in each case if vol. of container is 1L?

i $V = 1L$, $K_c = 4$, no. of moles = 2 each

	A	+ B	⇌ C	+ D
t=0	2	2	2	2
t=t	2-x	2-x	2+x	2+x

$[A] = 2 - \frac{2}{3} = \frac{4}{3}M$ $\frac{(2+x)^2}{(2-x)^2} = 4$

$[B] = \frac{4}{3}M$ $\frac{2+x}{2-x} = 2$

$[C] = \frac{8}{3}M = [D]$ $\boxed{x = 2/3}$

ii $A + B \rightleftharpoons C + D$

$[M] = 2$

iii $A + B \rightleftharpoons C + D$

	A	B	C	D
t=0	2	2	2	2
t=t	2+x	2+x	2-x	2-x

$$\frac{1}{4} = \left(\frac{2-x}{2+x}\right)^2$$

$$x = 2/3$$

$A + B \rightleftharpoons 2C$ at 300°C, moles of A, B, C are 2, 2, 3 moles respectively. If K_c at this temperature is 9; Volume = 1 L

i In which direction will the equilibrium more.

ii What will be equilibrium conⁿ of A, B, C ?

Ans:- i $Q_c = \frac{[C]^2}{[A][B]'} = \frac{9}{4}$

$K_c = 9$

As $K_c > Q_c$

∴ The reaction will more in forward direction.

ii Equilibrium Conⁿ of [A] =

$A + B \rightleftharpoons 2C$

	A	B	2C
t=0	2-x	2-x	3+2x

$$\left(\frac{(3+2x)^2}{(2-x)^2}\right) = 9$$

$$x = 3/5$$

$A = 7/5$

$B = 7/5$

$C = 21/5$

iii) If $\frac{4}{5}$ moles of C is added; what will be the new equilibrium Concⁿ ? V= 1L.

Ans iii)

$$A + B \rightleftharpoons 2C$$

$$\tfrac{7}{5} \qquad \tfrac{7}{5} \qquad \tfrac{21}{5}+\tfrac{4}{5}=5$$

$$Q_c = \frac{[5]^2}{(7/5)^2} = \frac{25}{(7/5)\cdot(7/5)} > K_c$$

$$Q_c > K_c$$

∴ It will move in the backward direction

$$A + B \rightleftharpoons 2C$$

$$\tfrac{7}{5}+x \qquad \tfrac{7}{5}+x \qquad 5-2x$$

$$\Rightarrow \left(\frac{5-2x}{\frac{7}{5}+x}\right)^2 = 9$$

$$\Rightarrow (5-2x) = \left(\tfrac{7}{5}+x\right)9$$

$$5(5-2x) = 7+5x \cdot 9$$

$$x = \frac{4}{25}$$

$$\therefore [A] = \tfrac{7}{5}+\tfrac{4}{25} = \frac{39}{25}\,M$$

$$[B] = \tfrac{7}{5}+\tfrac{4}{25} = \tfrac{31}{25}\,M$$

$$[C] = \frac{125}{25} - \tfrac{8}{25} = \frac{117}{25}\,M$$

If Value of "K" is very large; $(K > 10^3)$

$$R \longrightarrow P$$

$$K = \frac{[P]}{[R]}$$

$$[P] >> [R]$$

$$[P] + [R] \approx [P]$$
$$[P] - [R] \approx [P]$$

We will solve question assuming forward reaction by limiting reagent concept.

✳ When value of "K" is very small; $(K < 10^{-3})$

$$R \longrightarrow P$$
$$K = \frac{[P]}{[R]}$$
$$[R] \gg [P]$$
$$[R] \pm [P] \approx [R]$$

$p^H = -\log[H^+]$. What will be p^H of 0.1M CH_3COOH ? Given equi^m constant for

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

is $K_c = 10^{-5}$?

Ans:-

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$t=0$ 0.1

$t=t$ $0.1-x$ x x

$$K = 10^{-5} = \frac{x^2}{0.1-x} = \frac{x^2}{0.1}$$
$$x = 10^{-3}$$
$$[x^+] = x = 10^{-3}$$
$$p^H = -\log_{10}[10^{-3}]$$
$$\boxed{p^H = 3}$$

$2O_3 \rightleftharpoons 3O_2$. If $K_p = 10^8$ At eq^m total pressure is 10 atm. What will be partial pressure of each gas?

Ans:- $2O_3 \rightleftharpoons 3O_2$

P 10

$$\frac{10^3}{P^2} = 10^8 \Rightarrow P = 10^{-5/2}$$

As Kp is very Large. Thus the rxn moves towards forward directions.

$P_{O_3} + P_{O_2} = 10$ atm

ACTIVE MASS

$\propto$ Concentration

$\propto$ Partial pressure

Reaction are of two types:-

1. HOMOGENOUS REACTION

All reactants, products, catalysts; all should be in same phase, All gases and aqueous solution, uniformly distributed system in single phase.

2. HETROGENOUS REACTION

Reactants, products, catalysts may be in two or more than two phases These type of reaction are called hetrogeneous reaction.

All solids and liquids are in different phases.

eg:- $SO_{2(g)} + \frac{1}{2}O_{2(g)} \overset{NO(g)}{\rightleftharpoons} SO_{3(g)}$

Homogenous

$SO_{2(g)} + \frac{1}{2}O_{2(g)} \overset{Pt(s)}{\rightleftharpoons} SO_{3(g)}$

Hetrogeneous

$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

↑

Hetrogenous

There are 3 Phases because solids are taken in different phases along with CO_2 gas.

$NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$

Hetro (2 phases)

$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOC_2H_{5(aq)} + H_2O_{(aq)}$

same phase(aq.) ; Homogeneous

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Homogeneous

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

? $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$t=0$ $\quad a \qquad b$

$t=t$ $\quad a-x \qquad b-3x \qquad 2x$

$$K_c = \frac{\left[\frac{2x}{V}\right]^2}{\left[\frac{b-3x}{V}\right]^3\left[\frac{a-x}{V}\right]}$$

$$= \frac{\frac{4x^2}{V^2}}{[b-3x]^3 \cdot [a-x] \cdot \left[\frac{1}{V^{\text{[illegible]}}}\right]}$$

$$K_c = \frac{4x^2 V^2}{[b-3x]^3\,[a-x]}$$

$$K_p = \frac{[P_C]^2}{[P_B]^3 \cdot [P_A]^1}$$

Total moles $= a+b-2x$

Mole fraction of $NH_3 = \frac{2x}{a+b-2x}$

Mole fraction of $H_2 = \frac{b-3x}{a+b-2x}$

Mole fraction of $N_2 = \frac{a-x}{a+b-2x}$

$$K_p = \frac{\left[\frac{2x}{a+b-2x}\right]^2}{\left[\frac{b-3x}{a+b-2x}\right]^3\left[\frac{a-x}{a+b-2x}\right]}$$

$$K_p = \frac{[4x^2]\,[a+b-2x]^2}{(b-3x)^3\,(a-x)\,P_T^2}$$

DEGREE OF DISSOCIATION

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

	$2NH_3$	N_2	$3H_2$
$t=0$	a		
$t=t$	$a-2x$	x	$3x$

$$a \longrightarrow 2x$$

$$1 \longrightarrow \frac{2x}{a} = \alpha$$

$$x = \frac{a\alpha}{2}$$

$$= a-2\left(\frac{a\alpha}{2}\right) \qquad \frac{a\alpha}{2} \qquad \frac{3\alpha a}{2}$$

$$= a(1-\alpha) \qquad \frac{a\alpha}{2} \qquad \frac{3a\alpha}{2}$$

$$n_T = a(1-\alpha) + \frac{a\alpha}{2} + \frac{3a\alpha}{2}$$

$$= a(1+\alpha)$$

$$P_{NH_3} = \frac{a(1-\alpha)}{a(1+\alpha)} P_T$$

$$P_{N_2} = \frac{a\,\alpha/2}{a(1+\alpha)} P_T$$

$$P_{H_2} = \frac{3a\,\alpha/2}{a(1+\alpha)} P_T$$

$$\therefore K_p = \frac{(N_2)^1 \, (H_2)^3}{(NH_3)^2}$$

$$\frac{\left(\frac{\alpha/2}{1+\alpha}\right)\left(\frac{\alpha/2}{1+\alpha}\right)^3 P_T^4}{\left(\frac{1-\alpha}{1+\alpha}\right)^2 P_T^2}$$

$$\boxed{K_p = \frac{27}{16} \cdot \frac{\alpha^4}{(1-\alpha^2)^2} P_T^2}$$

$\alpha <<< 1$

$$\left.\begin{matrix} 1-\alpha \\ 1+\alpha \end{matrix}\right. \simeq 1$$

"K" is small

$R \rightleftharpoons P$

$K < 10^{-3}$

$$K_c = \frac{[P]}{[R]}$$

$[R] >>> [P]$

$[R] + [P] \approx [R]$

$[R] - [P] \approx [R]$

"K" is Large

$R \rightleftharpoons P$

$K > 10^{3}$

$$K_c = \frac{[P]}{[R]}$$

$[P] >>> [R]$

$[R] + [P] \approx [P]$

$[R] - [P] \approx [P]$

$2A + 3B \rightleftharpoons 3C + 2D$

Initially 3 moles of A, 8 moles of B, is given, If volume of container is 2L, value of K_c is 10^6, then calculate conc^n of $[A], [B], [C], [D] = ?$

$2A + 3B \rightleftharpoons 3C + 2D$

$t=0$ 3 8

$t=t$ $3-2x$ $8-3x$ $3x$ $2x$

Value of K_c is very Large $> 10^3$

$$[P] \gg [R]$$

$$[A] = \left[\frac{3-2x}{2}\right]^2$$

$$[B] = \left[\frac{8-3x}{2}\right]^3$$

$$[C] = \left[\frac{3x}{2}\right]^3$$

$$[D] = \left[\frac{\cancel{2}x}{\cancel{2}}\right]^2$$

Ans:-

$2A + 3B \rightleftharpoons 3C + 2D$

$t=0$ 3 8

$t=t$ $\overset{L.R = A}{x}$ $8-\frac{9}{2}$ $\frac{9}{2}$ $= 3$

$= \frac{7}{2}$ $\frac{9}{2}$ 3

$$10^6 = \frac{\left(\frac{9}{2}\right)^3 \cdot (3)^2}{\left(\frac{7}{2}\right)^3 \cdot (x)^2}$$

$$x = \sqrt{\frac{\left(\frac{9}{2}\right)^3 \cdot (3)^2}{\left(\frac{7}{2}\right)^3} \times 10^{-6}}$$

$$x = \sqrt{\frac{27 \times 9}{343} \cdot 10^{-6}}$$

$$\boxed{x = \frac{27}{7} \times \frac{3}{\sqrt{7}} \times 10^{-3}}$$

For Calculation of Conc^n of L·R ; value of K_c will be provided, when K_c is Large.

$$[C] = \frac{9}{2} \times \frac{1}{2}\,M$$

$$[D] = \frac{3}{2}\,M$$

$$[B] = \frac{7}{2} \times \frac{1}{2} = \frac{7}{4}\,M$$

$$[A] = \frac{27 \times 3}{7\sqrt{7}} \times 10^{-3}\,M$$

→small

HETROGENOUS EQUILIBRIUM

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

- Density of solids is constant at constant temperature.
- On increasing temperature, the density of solids as well as liquids will decrease due to volume expansion.

$$\text{Conc}^n = \frac{\text{Mole}}{\text{Volume}}$$

$$\text{Mole} = \frac{\text{Given mass}}{\text{Mole. mass}}$$

$$\therefore \text{Conc}^n = \frac{\text{Mass}}{M \cdot V}$$

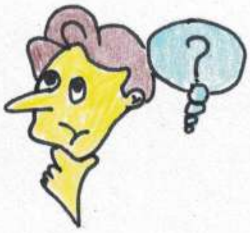
$$\text{Conc}^n = \frac{d}{M}$$

Therefore, concentration of the solids remains constant as density as well as molecular weight remains constant.

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

$$K = \frac{[CaO].[CO_2]}{[CaCO_3]}$$

$$\boxed{K_c = [CO_2]}$$



200g $CaCO_3$ is taken in a 1L container At 300K, 50% $CaCO_3$ gets dissociated a/c to equilibrium.

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

i What will be the value kp and K_c ?

ii After getting equilibrium, if we'll get add 50g $CaCO_3$, what will be concn of CO_2 ?

	$CaCO_{3(s)}$	$\rightleftharpoons$ $CaO_{(s)}$	+ $CO_{2(g)}$
t=0	2		
t=t	2-x	x	x
	2-1	1	1

i

$K_c = [CO_2]$

$K_c = 1\ mol/l$

ii No change

$P = C \cdot R \cdot T$

$P = 1 \times \frac{1}{12} \times 300$ $\{ [CO_2] = 1 \}$

$\boxed{K_p = 25 \text{ atm}}$

iii If Concⁿ of CO_2 is 1 mol/l in the above equilibrium, in which direction will eqᵐ go when we add 50g CaO solid?

No change in the pathway.

iv what will happen when this eqᵐ mixture is put into 1.5 l container

No change in the K_c as $K_c \propto T$.

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

$K_c = 1$

$Q_c = \frac{1}{3/2} = 2/3$

$Q_c < K_c$

∴ It goes in forward direction.

v How much amount is gone forward?

$$\begin{array}{ccccc} CaCO_{3(s)} & \rightleftharpoons & CaO_{(s)} & + & CO_{2(g)} \\ 1-x & & 1+x & & 1+x \end{array}$$

$\left[\frac{1+x}{1.5}\right] = 1$ $\left\{ \text{As } K_c \text{ only depends on } [CO_2] \right\}$

$$\begin{array}{ccccc} CaCO_{3(s)} & \rightleftharpoons & CaO_{(s)} & + & CO_{2(g)} \\ 1/2 & & 3/2 & & 3/2 \end{array}$$

VI When eq^m mixture is put into 0.5 l mixture?

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

It goes in the backward direction

$$\begin{array}{ccccc} CaCO_{3(s)} & \rightleftharpoons & CaO_{(s)} & + & CO_{2(g)} \\ 1+x & & 1-x & & 1-x \end{array}$$

$$\left[\frac{1-x}{1/2}\right] = 1$$

$$x = 1/2$$

$$\therefore \begin{array}{ccccc} CaCO_{3(s)} & \rightleftharpoons & CaO_{(s)} & + & CO_{2(g)} \\ 3/2 & & 1/2 & & 1/2 \end{array}$$

VII When eq^m mixture is put into 3L container?
pressure = ?

$$CaCO_{3(s)} \rightleftharpoons CaO + CO_{2(g)}$$

The eq^m goes into the forward direction.

$$\begin{array}{ccccc} CaCO_{3(s)} & \rightleftharpoons & CaO_{(s)} & + & CO_{2(g)} \\ 1-x & & 1+x & & 1+x \end{array}$$

$$\left[\frac{1+x}{3}\right] = 1$$

$$\boxed{x = 2}$$

This reaction is not possible

$\therefore$ Max x possible $x = 1$

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

$$\begin{matrix} 0 & & 2 & & 2 \end{matrix}$$

eqm is finished

For CO_2 gas

$$PV = nRT$$

$$P = \frac{\cancel{2}}{3} \times \frac{1}{\cancel{12}_{\cancel{6}\ 1}} \times \overset{50}{\cancel{300}}$$

$$\boxed{P = \frac{50}{3}\ \text{atm}}$$

SHORTCUT

▷ $$NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$$

$$P_T = P$$

$$\begin{matrix} P/2 & & P/2 \end{matrix}$$

$$K_p = P/2 \times P/2 = \frac{P^2}{4}$$

▷ $$A_2B_{(s)} \rightleftharpoons 2A_{(g)} + B_{(g)}$$

$$\begin{matrix} 2P/3 & & P/3 \end{matrix}$$

$$K_p = \left(\frac{2P}{3}\right)^2 \cdot \left(P/3\right)$$

$$K_p = \frac{4P^3}{27}$$

Question:- $A_2B_3 \rightleftharpoons 2A_{(g)} + 3B_{(g)}$

$P_T = P \qquad K_p = ?$

Answer:- $\left(\frac{2P}{5}\right)^2 \cdot \left(\frac{3P}{5}\right)^3$

$$= \frac{27 \times 4}{25 \times 125} \times P^5$$

$$\boxed{K_p = \frac{108}{3125} \times P^5}$$

Revision

Chemical equilibrium

$N_2O_4 \rightleftharpoons 2NO_2 \qquad \alpha = 0.5$ find $V.D_{min} = ?$

Ans:- $N_2O_4 \rightleftharpoons 2NO_2$

$t=0 \quad 1$

$t=t \quad 1-\alpha \qquad 2\alpha$

$$1 \times 92 = (1+\alpha) \cdot M_{min}$$

$$\frac{92}{1.5} = M_{min}$$

$$\therefore \boxed{VD_{mix} = \frac{92}{3}}$$

Que:- $N_2O_4 \rightleftharpoons 2NO_2$ Initial pressure in container = 600 atm, find pressure = 800 atm, find kp = ?

Ans:- As volume and temp. is fixed, therefore $\boxed{P \propto n}$, we can assume the initial mole as 600.

$$N_2O_4 \rightleftharpoons 2NO_2$$

t=0 600

t=t 600-p 2p

$600-p \rightarrow$ 400 atm

$2p \rightarrow$ 400 atm

$$600 - p + 2p = 800$$

$$P = 200 \text{ atm}$$

$$\therefore k_p = \frac{P_{NO_2}}{P_{N_2O_4}} = \frac{(400)^{\cancel{2}}}{\cancel{400}} = 400 \text{ atm.}$$

Le Chatelier's Principle

If chemical reaction is at eqm; on applying strain (change in pressure/ volume/temp. etc); the equilibrium will oppose that strain and goes in that direction in which strain is nullified.

Effect of concentration - An increasing concn eqm will shift towards opposite direction.

$$A \rightleftharpoons B$$

$$K_c = \frac{[B]}{[A]}$$

i On increasing [A];

i.e $[A] > [A]$

$Q_c < K_c$

forward direction

ii on increasing [B];

i.e $[B] > [B]$

$Q_c > K_c$

Backward direction

effect of Volume

- on increasing volume, eqm will shift towards number of gaseous moles are more.

i

$$\underset{a}{A} \rightleftharpoons \underset{b}{B} + \underset{c}{C}$$

$$K_c = \frac{bc}{aV}$$

$$Q_c = \frac{bc}{aV'}$$

$V' > V$

$Q_c < K_2$

Forward direction

ii

$$\underset{a}{A} + \underset{b}{B} \rightleftharpoons \underset{c}{C}$$

$$K_c = \frac{cV}{ab}$$

$$Q_c = \frac{cV'}{ab}$$

$V' > V$

$Q_c > K$

Backward direction

$\Delta n > 0$ Forward

$\Delta n < 0$ Backward

$\Delta n = 0$ No effect

Effect of Pressure

- on increasing pressure on eqm, it will shift towards that direction where no. of gaseous moles are less.

Equilibrium is established at constant temperature. So, we can apply Boyl's Law.

$$P \propto \frac{1}{V}$$

$\Delta n > 0$ Backward

$\Delta n < 0$ Forward

$\Delta n = 0$ No effect

eg:-

$$A_{(g)} + 2B_{(g)} \rightleftharpoons 3C_{(g)} + D_{(g)}$$

$\Delta n = 4-3 = 1$

$\Delta n > 0 \longrightarrow$ Backward

(gas which is non reactive with eqm)

Effect of Addition of Inert gas

- Inert gas is a gas which is non reactive with eqm.

a. At Constant volume

There will be no effect at equilibrium.

Let us suppose in a close container (A, B, C) are in equilibrium.

$$A \rightleftharpoons B + C$$

$t = t \quad a \qquad b \qquad c$

$$K_p = \frac{P_B \cdot P_C}{P_A} \; ; \quad P_T = (a+b+c) \cdot \frac{RT}{V}$$

$$P_A V = aRT$$

$$P_B V = bRT$$

$$P_C V = cRT$$

Now add an inert gas "D" (moles = "d"), then total pressure will increase but partial pressure of individual gases remains same.

$$P_T = P_A + P_B + P_C + P_D$$

$$P_T \cdot V = (a+b+c+d)\,RT$$

$$P_T = (a+b+c+d) \cdot \frac{RT}{V}$$

$$P_A = \frac{a}{a+b+c+d} \cdot P_T$$

$$P_A = \frac{a}{(a+b+c+d)} \cdot (a+b+c+d) \cdot \frac{P_T}{V}$$

$$\boxed{P_A = \frac{aRT}{V}}$$ Similarly. For all.

∴ There is no effect of adding inert gas at const. volume.

b. At Constant Pressure

Effect will be same as increase in volume.

i.e:- $\Delta n > 0$ forward

$\Delta n < 0$ backward

$\Delta n = 0$ no effect

Effect of Catalyst

– catalyst are substances which can accelerate or retard the chemical reaction OR Catalyst can make rate of reactions faster or slower.

There will be no effect at equilibrium conc^n on addition of catalysts. eq^m may be reached earlier with the help of catalyst.

Effect of Temperature

Types of reactions:-

(i) Exothermic Reaction

The Reaction in which heat is ejected are called exothermic reaction.

$$A \rightleftharpoons B + q\ Cal$$

$$\Delta H < 0$$

(ii) Endothermic Reaction

The Reaction in which heat is absorbed.

$$A + q\ Cal \rightleftharpoons B$$

$$\Delta H > 0$$

Gibb's Free energy

$$\Delta G = \Delta H - T.\ \Delta S$$

ΔH = Enthalpy

T = Temp. of reaction

ΔS = change in entropy

Standard Conditions

25°C temperature, 1 atm pressure, concentration of species = 1M

$$\Delta G^\circ = \Delta H^\circ - T.\ \Delta S^\circ$$

At Standard Cond^n Gibb's free energy

$$\boxed{\Delta G = \Delta G^\circ + RT \ln Q}$$

ΔG = Gibb's free energy at a temperature
ΔG° = Gibb's free energy at a standard
Q = Reaction Quotient

$\Delta G < 0$ system (process) is feasible
$\Delta G > 0$ Process is non feasible
$\Delta G = 0$ process is at equilibrium

At equilibrium,

$$\Delta G = 0;$$

$$\Delta G^\circ + RT \ln Q = 0$$

$$-RT \ln Q = \Delta G^\circ \text{ — ①}$$

$$\Delta G^\circ = \Delta H - T.\Delta S^\circ$$

At equilibrium $K_c = K_p = Q_c$

From ①

$$-RT \ln K_c = \Delta H^\circ - T.\Delta S^\circ$$

Concn of the products is more than the concn of the reactants; thus, the equilibrium will shift towards endothermic direction.

eg:- (i) $A \rightleftharpoons B$ $\Delta H > 0$

It's endothermic on increasing temp, eqm reaction goes in the forward direction.

(ii) $A \rightleftharpoons B$ $\Delta H < 0$

It's exothermic on increasing temp, eqm shifts in the backward direction.

Ex:- $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $(\Delta H < 0)$

Δn is negative

∴ The reaction goes in backward direction originally but we want more production of NH_3. Therefore, the volume must be decreased pressure must be increased, temperature must be Lowered, concn of N_2 and H_2 must be high so that the reaction moves in the forward direction.

PHYSICAL EQ^{M}

In this Section, we'll discuss eq^m in which physical state will be changed.

Melting of Solids

$$\text{Solid} \rightleftharpoons \text{Liquid}$$

There are two types of solids

(i) $d_{solids} < d_{Liquids}$ eg:- Water and ice

(ii) $d_{solids} > d_{Liquids}$ eg:- Any Solid

a. WATER

$$\text{Ice} \rightleftharpoons \text{Water}$$

$$\Delta H > 0$$

Volume of Ice will be greater than V_{H_2O}, for same mass because $d_{ice} < d_{H_2O}$. Hence, on high pressure eq^m will shift towards right. This is endothermic reaction, so, on high temp, eq

Melting of ice will be favourable on high temp and high pressure.

$$\text{Ice} \rightleftharpoons \text{Water} \qquad \Delta H > 0$$

on increasing temp, we get more H_2O.

$$P \propto \frac{1}{V}$$

Volume of Ice is more, therefore pressure must be high (Vol. of H_2O is less)

For Vol, temp ↑

b. SOLID

$$A_{(s)} \rightleftharpoons A_{(l)} \qquad (\Delta H > 0)$$

For solid A, density in liquid state will be less, so vol. of A in its liquid state will be more so eq^m will shift towards right on Low pressure and high temp.

c. LIQUID ⇌ VAPOUR eq^m

(i) Vapour Pressure

It is the pressure exerted by the vapour on its own Liquid when Liquid is in eq^m with vapour.

Vapour Pressure only depends on temperature

$$\log\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Where P_1 is V.P at temp. T_1 and P_2 is V.P at temp. T_2.

Vapour Pressure doesn't depend on amount of Liquid.

Question:- To an evacuated vessel with a movable piston under external pressure of 1 atm 0.1 mole of He and 1 mole of unknown compound (V.P = 0.68 atm at 0°c) are introduced, considering the ideal gas behaviour find total volume of gaseous mixture at 0°C.

Answer:- For unknown compound

$$0.68 \times V = 1 \times \frac{1}{12} \times 273$$

$$V = \frac{273 \times 100}{68 \times 12}$$

For He gas,

$P = 0.32$, $V = ?$, $n = 0.1$, $R = 1/12$, $T = 273$

$P_T = 1$ atm

$\therefore P_{He} = 0.32$ atm

$$0.32 \times V = 0.1 \times \frac{1}{12} \times 273$$

$$V = \frac{22.4 \times 0.1}{0.32} = 7\,l$$

Question:- A gaseous mixture of He and $H_2O_{(g)}$ in a VL container has a total pressure of 2.1 atm (V.P of H_2O is 0.1 atm). Find the total pressure of gaseous mixture if it is completelly transfered to:-

(i) $V/3$ L

(ii) 3VL

Answer:- Pressure of water will remain constant when we change the vol. of the Container only the pressure exerted by "He" gas changes.

(i) $P_1V_1 = P_2V_2$

$2 \times \cancel{V} = P_2 \times \cancel{V}/3$

$\boxed{P_2 = 6 \text{ atm}}$ $\therefore T_P = P_2 + 0.1 = 6.1$ atm

(ii) $P_1V_1 = P_2V_2$

$2 \times \cancel{V} = (3\cancel{V}) \cdot P_2$

$$\boxed{P_2 = \frac{2}{3}}$$

$\therefore T_P = \frac{2}{3} + 0.1$ atm

VP only depend on temperature

Relative Humidity

$$\boxed{RH = \frac{\text{V.P of water}}{\text{Saturated V.P}}}$$

Pressure of Dry air } $\quad P_{\text{moist air}}$ – Aqueous tension

$P_{\text{moist air}}$ – VP_{water}

Ans:- $P_{sat} = \frac{22.8}{760}$

$P_{H_2O} = 10^{-2}$ atm

$R_H = \frac{10^{-2} \times 760}{22.8}$

$R_H = 1/3$

To $CuSO_4 \cdot 5H_2O$ to lose water, the eq^m must go in the forward direction.

$$\boxed{R_H < 1/3}$$

Solubility of a gas in Liquid

$$A_{(g)} + B_{(l)} \rightleftharpoons A_{(al)}$$

$\Delta H < 0$, If temp is ↑, it will go in backward direction; therefore, solubility ↓

Henry's Law :- Solubility of a gas in a liquid depends on the Partial Pressure of the gas over the Liquid.

$$x_{gas} = \frac{n_g}{n_g + n_l}$$ {As n_g is very small}

$$P_{gas} \propto x_{gas}$$

$$P_{gas} = K_H \cdot x_{gas}$$

$$\therefore x_{gas} \approx \frac{n_g}{n_l}$$

$$\boxed{\therefore P_{gas} = K_H \cdot \frac{n_g}{n_l}}$$

Question

The Henry constant of solubility of N_2 in H_2O at 298k is 10^5 atm. The mole fraction of N_2 in air is 0.8. Find out the amount of N_2 dissolved in 10 mole of H_2O at 5 atm.

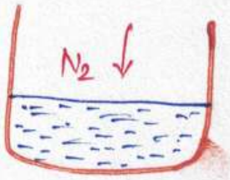
Answer

$K_H = 10^5$, $T = 298\,K$

$n_{N_2} = 0.8$, $n_{H_2O} = !$

It can't be used as it is in air, Not dissolved

Total mole of H_2O = 10 mol



$P = 5\,atm$ $n_{N_2} = 0.8$

$\therefore P_{N_2} = 0.8 \times 5 = 4\,atm$

$P_{N_2} = K_H = \frac{n_{N_2}}{10}$

$$4 = 10^5 \cdot \frac{n_{N_2}}{10}$$

$$\boxed{n_{N_2} = \frac{4}{10^4}}$$