CHEMICAL EQUILIBRIUM

Types of reac$^{\underline{n}}$:-

(I) On the basis of state :

(a) Homogeneous

Reactant & product in same state

* $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_3(g)$

(b) Heterogeneous

Reactant & product in diff state

* $CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_2(g)$

(II) On the basis of heat :

(a) Exothermic

* heat evolved

$A \longrightarrow B$; $\Delta H = -ve$ } New convection.

$A \longrightarrow B + q$ } old convection.
$A - q \longrightarrow B$

* eg : Combustion reac$^{\underline{n}}$
Neutralization reac$^{\underline{n}}$
Formation reac$^{\underline{n}}$ (generally)

exception :-

$\left\{ \begin{array}{l} N_2 + O_2 \longrightarrow 2NO/N_2O_5/N_2O_4 \\ O_2 + F_2 \longrightarrow OF_2/O_2F_2 \end{array} \right\}$

||
ENDOTHERMIC

(b) Endothermic.

* heat absorbed.

$A \longrightarrow B$; $\Delta H = +ve$ }

$A + q \longrightarrow B$ } old convection
$A \longrightarrow B - q$

* eg : Dissociation reac$^{\underline{n}}$
Phase transformation
→ fusion (S→L)
→ vapourisation (L→G)
→ sublimation (S→G)

III On the basis of direction :-

ⓐ Reversible	ⓑ Irreversible
* $R \rightleftharpoons P$	* $R \longrightarrow P$
* Bidirectional	* Unidirectional
* Equilibrium is achieved	* Equilibrium not attained.
* They donot proceed to completion	* They proceed in completion
* Closed container	* Open container.
eg SA+WB Weak acid + Strong base. WA+WB	eg SA+SB.

⇒ ACTIVE MASS :- (denoted by [ ])

Active mass is the concentration expressed in molarity.

$$\text{Active mass} = \frac{\text{no of moles substance}}{\text{volume in L}}$$

$$= \frac{n}{V}$$

$$= \frac{w}{\text{Mwt} \times V}$$

$$= \frac{\rho}{\text{Mwt}} = \frac{\text{Density}}{\text{Molar mass}}$$

* Active mass in different cases :-

① Solid :-

[solid] = const

[solid] = 1

② Liquid :-

[Liquid] = const = 1

③ Gas :-

[Gas] = concentration = $\frac{n}{V}$ or [Gas] = Pressure

$PV = nRT$

$P = \left(\frac{n}{V}\right)RT \quad P = CRT \quad [P \propto C] \quad$ Active mass $\propto C \propto P$

* For solid and Liquid active mass is const and is assumed to be '1' as their density and Molar mass is const.

Q Calculate the active mass in each case.

(i) 36 g of Graphite.

(ii) 2 mol of NaCl(s) in 10L volume

(iii) 6×10^{20} molecule of O_2 gas in 10L vessel.

(iv) 2g of H_2 gas in 500ml vessel

Soln

1. Graphite → Solide active mass = 0 = 1
2. 2 mol NaCl(s) → solid active mass = 1
3. $\frac{6 \times 10^{20}}{6 \cdot \times 10^{23}} = n = 10^{-3} \quad C = \frac{10^{-3}}{10} = 10^{-4} M = [O_2]$
4. $\frac{2}{2} = n = 1$. $\quad C = \frac{1}{\cancel{500}} \times \overset{2}{\cancel{1000}} = 2 = [H_2]$

⇒ PARTIAL PRESSURE :-

* Indivisual pressure of gas in a gaseous mixture is known as partial pressure.

[Partial pressure of gas = total pressure x Mole fraction of gas]

$$\boxed{P = P_T \times X} \qquad X = \frac{\text{mole of component}}{\text{total moles}}$$

* $\boxed{\begin{matrix} \text{gas}A & \text{gas}B \\ n_A & n_B \end{matrix}}$ P_T = total pressure

$P_A = P_T \times X_A$ $\qquad$ $P_B = P_T \times X_B$

$$\left[P_A = P_T \times \left(\frac{n_A}{n_A + n_B}\right)\right] \qquad \left[P_B = P_T \times \left(\frac{n_B}{n_A + n_B}\right)\right]$$

* Ratio of moles = Ratio of partial pressure $\left\{\frac{P_A}{P_B} = \frac{n_A}{n_B}\right\}$

Q. Calculate the partial pressure in each case

(1) 2g ~~molecules~~ of H_2 gas is mixed with 32g of CH_4 gas such that total pressure of system is P

$$P_{H_2} = P \times \left(\frac{\frac{2}{2}}{\frac{2}{2} + \frac{32}{16}}\right) = P\left(\frac{1}{1+2}\right) = P/3$$

$$P_{CH_4} = P \times \left(\frac{2}{1+2}\right) = 2P/3$$

(11) 3×10^{23} molecules of O_2 gas is present with 2g of H_2 gas such that total pressure is 9 atm

$$P_{O_2} = 9\times\left(\frac{\frac{3\times10^{23}}{6\times10^{23}}}{\frac{1}{2}+1}\right) = 9\left(\frac{\frac{1}{2}}{\frac{1}{2}+1}\right) = 9\left(\frac{\frac{1}{2}}{\frac{3}{2}}\right) = 9/3 = 3\text{ atm}$$

$$P_{H_2} = 9\times\left(\frac{1}{\frac{1}{2}+1}\right) = 9\left(\frac{1}{3/2}\right) = \frac{\overset{3}{\cancel{9}}\times2}{\cancel{3}} = 6\text{ atm}$$

⇒ Law of mass action :-

* Given by Guldberg and Waage

* Acc to this law rate of chemical reacⁿ is directly proportional to multiplication of active mass of reactant with each raised to the power of their stichometric coefficient

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

$$r \propto [A]^a \times [B]^b$$

$$r = K[A]^a \times [B]^b$$

[A], [B] = active mass

a, b = stichometric coefficient of A and B.

r = rate of reacⁿ

K = rate const

→ Temp

→ Catalyst

eg :- $A + 2B \longrightarrow C$

$$r_f = k_f[A]^1[B]^2$$

Q Consider a reacⁿ $2A + \frac{1}{2}B \longrightarrow 3C$. If conᶜ of A is unchanged and that of is made 4 times.. Then what would be the rate of reacⁿ

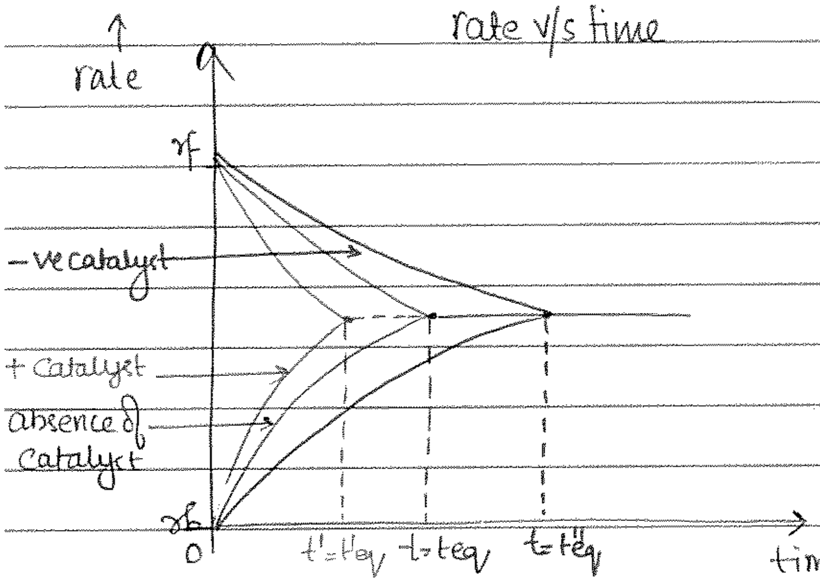
Solⁿ $r_1 = K_f[A]^2[B]^{1/2}$ $r_2 = k_f[A]^2[4B]^{1/2} \Rightarrow r_2 = 2r_1$

⇒ EQUILIBRIUM :-

* At equilibrium rate becomes equal
$r_f = r_b$

* Concentration of Reactant and product becomes const with time

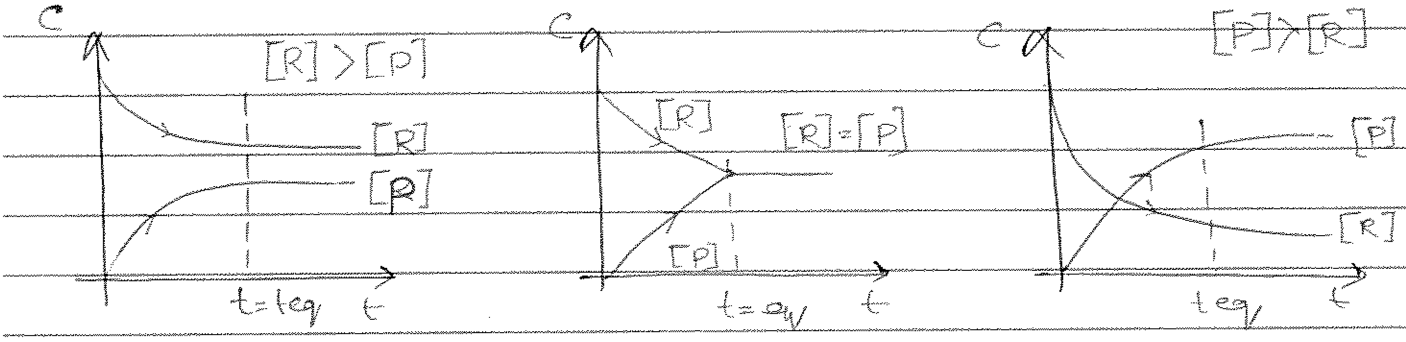
rate v/s time



⇒ Characteristics of equilibrium :-

* Rate must be equal & concⁿ of reactant & product must be constant with time.

concⁿ v/s time



- * Chemical equilibrium is dynamic in nature.
- * All the measurable properties like pressure, con^{c}, temp, mole, colour etc become const with time at equilibrium
- * catalyst do not affect the equilibrium. It helps in attaining the equilibrium rapidly by lowering down the activation energy.

- * Equilibrium can be achieved from both sides of reac^{n}. (from Reactant to product OR product to Reactant)

- * Equilibrium is achieved in a closed container.

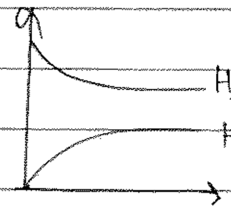
Q. Select the statement which is correct and incorrect?

① Rate must be equal ✓
② conc must be equal X
③ conc may be const with time. X
④ conc may be equal. ✓
⑤ Reac^{n} is 50% complete when eq attained X

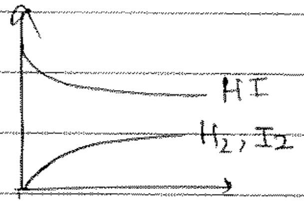
Q. Which con^{n} v/s time curve is correct for reac^{n}

$$H_2 + I_2 \rightleftharpoons 2HI$$

(I) ✓

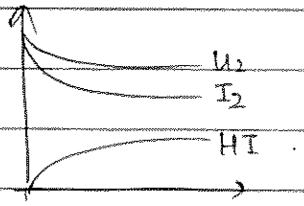


(III) ✓

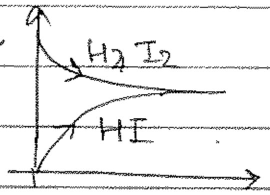


(Reac^{n} in backward reac^{n})

(II)



(IV) ✓



Sol^n $H_2 + I_2 \rightleftharpoons 2HI$.

$t=0$ a a 0.

$a-x$ $a-x$ $2x$. } 1st graph correct .

∫ $a-x = 2x$

$x = a/3$

$2a/3$ $2a/3$ $2a/3$ } 4th graph correct .

$H_2 + I_2 \rightleftharpoons 2HI$

$t=0$ 0 0 a

$t=t$ x x $a-2x$ } 3rd graph correct (Backward reac^n)

⇒ Derivation of Equilibrium const :-

Consider a reversible reac^n

$$aA + bB \underset{r_b}{\overset{r_f}{\rightleftharpoons}} cC + dD$$

$$r_f = k_f [A]^a [B]^b$$

$$r_b = k_b [C]^c [D]^d$$

At equilibrium $r_f = r_b$

$$k_f [A]^a [B]^b = k_b [C]^c [D]^d$$

$$\frac{k_f}{k_b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} = K_c \qquad \boxed{K = \frac{k_f}{k_b}}$$

forward rate const

backward rate const

$$\boxed{K = \frac{[C]_e^c [D]_e^d}{[A]^a [B]^b}} \qquad K = \frac{\text{active mass of product}}{\text{active mass of Reactant}}$$

→ Different form of equilibrium const :-

K

- kc (Equilibrium const in terms of con^{c})
- kp (Equilibrium const in terms of partial pressure)

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

$[A]_e, [B]_e, [C]_e, [D]_e$ = con^{c} of A, B, C, D at equilibrium

$$\boxed{K_p = \frac{(P_C)_e^c\,(P_D)_e^d}{(P_A)_e^a\,(P_B)_e^b}}$$

$(P_A)_e, (P_B)_e, (P_C)_e, (P_D)_e$ = Partial pressure of A, B, C, D at equilibrium

* Heterogenous

→ equilibrium involving gases

- → gas → kp, → kc
- → [SOLID] = [LIQUID] = 1

* Homogenous

→ equilibrium

- → gas → kp, → kc
- → LIQUID → kc

[LIQUID] ≠ 1 .
= const .

Solution → active mass → concentration

eg $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_2(g)$

$kp = (P_{CO_2})^1$

$kc = [CO_2]^1$

Q. Write the expression of kp & kc

① $N_{2(g)} + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$kc = \frac{[NH_3]^2}{[N_2][H_2]^3}$ $kp = \frac{(P_{NH_3})^2}{(P_{H_2})^3(P_{N_2})}$

② $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

$kc = [CO_2][NH_3]^2$ $kp = (P_{CO_2})(P_{NH_3})^2$

③ $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$kc = \frac{[HI]^2}{[H_2][I_2]}$ $Kp = \frac{(P_{HI})^2}{(P_{I_2})(P_{H_2})}$

④ $C_2H_5OH_{(l)} + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

$kc = \frac{[H_2O][CH_3COOC_2H_5]}{[C_2H_5OH][CH_3COOH]}$ ~~$kp = (P_{H_2O})(P_{CH_3COOC_2H_5}$~~

Q Consider a reac$^{\underline{n}}$

$CuSO_4 . 5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$

If the pressure of water vapour is 10^{-1} atm at equilibrium then calculate kp

Sol$^{\underline{n}}$ $kp = (P_{H_2O})^5 = (10^{-1})^5 = 10^{-5}$ atm

Q. Consider a reac$^{\underline{h}}$

$$N_2O_{4(g)} \rightleftharpoons 2NO_2(g)$$

If at equilibrium total pressure is 10 atm and partial pressure of NO_2 is 6atm. Find kp.

Sol$^{\underline{n}}$ Total pressure = 10 atm.

$P(N_2O_4) + P_{NO_2} = 10$

$P_{N_2O_4} = 10 - 6 = 4$

$$kp = \frac{(P_{NO_2})^2}{P(N_2O_4)} = \frac{(6)^2}{4}$$

$$= \frac{\cancel{36}}{\cancel{4}} \; 9\,\text{atm}$$

Q In a 10L vessel, 300 gm of $CaCO_3$ decomposes to give CaO & CO_2 such that at equilibrium 55 gm CO_2 gas is present. Calculate the value of kc

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$kc = [CO_2] = \frac{\overset{5}{\cancel{55}} \times}{4\,\cancel{44} \times 1\cancel{0}\,2} = \frac{1}{8}\,M = 0.125\,M$$

Q. Consider a reac$^{\underline{n}}$ $A \rightleftharpoons 2B$. If $[A]_e = x$ then conc of B at equilibrium will be?

$$kc = \frac{[B]^2}{[A]} \qquad \frac{kf}{kb} = \frac{[B]^2}{[A]}$$

$$\frac{kf}{kb} \times x = [B]^2 = (kf\, kb^{-1} x)^{\frac{1}{2}} = [B]$$

:- Relation b/w kp and kc ⇒

$$\left[K_p = K_c (RT)^{\Delta n_g} \right]$$

kp, kc = equilibrium const in terms of pressure & concentration.

R = Gas const = 0.0821 L^{-1} atm mol^{-1} k^{-1}

T = Temp in Kelvin

Δn_g = (Sum of stichometric cofficient of gaseous product) − (sum of stichometric coefficient of gaseous reacⁿ).

eg :- ① $A(s) + 2B(g) \rightleftharpoons C(g) + D(l)$

$\Delta n_g = 1 - 2 = -1$

② $2A(g) + 3B(g) \rightleftharpoons 4(s)$

$\Delta n_g = 0 - 5 = -5$

unit of kp and kc

$k_p = (atm)^{\Delta n_g}$

$k_c \longrightarrow (M)^{\Delta n_g}$ or $\left(\frac{mol}{L}\right)^{\Delta n_g}$

* Deffrent cases on the basis of Δn_g :-

Case I $\Delta n_g = 0$

$\boxed{k_p = k_c}$

kp → unitless

kc → unitless

eg $H_{2(g)} + I_2(g) \rightleftharpoons 2HI(g)$

$\Delta n_g = 2 - 2 = 0$ kp = kc .

Case IInd :- $\Delta n_g > 0$

$k_p > k_c$

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

$\Delta n_g = 2-1 = 1$.

$\Delta n_g > 0$.

$k_p > k_c$.

$k_p \rightarrow atm$

$k_c \rightarrow M$.

Case IIIrd $\Delta n_g < 0$

$k_p < k_c$

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

$\Delta n_g = 2-4 = -2$

$\Delta n_g < 0$

$\boxed{k_p < k_c}$

$k_p = (atm)^{-2}$

$k_c = (molarity)^{-2}$

Case IVth :-

Special case At $T = \frac{1}{R} = \underline{\underline{12.18\,K}}$.

$k_p = k_c(RT)^{\Delta n_g}$ $\quad k_p = k_c\left(\cancel{R} \times \frac{1}{\cancel{R}}\right)^{\Delta n_g}$

$$\boxed{k_p = k_c}.$$

Value of kp is equal to value to kc whatever be the value of Δn_g.

* $\boxed{\frac{k_p}{k_c} = (RT)^{\Delta n_g}}$

* Relation b/w kp & kx :-

$k_p = k_x \times (P_T)^{\Delta n_g}$

k_x = equilibrium const in term of mole fraction

P_T = total pressure at equilibrium.

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

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$k_x = \frac{(X_B)^2}{(X_A)}$ $k_p = \frac{(P_B)^2}{P_A}$ $k_c = \frac{[B]^2}{[A]^1}$

Q For which reacⁿ kp = kc.

ⓐ $N_2 + 3H_2 \rightleftharpoons 2NH_3$ ⓑ $2SO_2 + O_2 \rightleftharpoons 2SO_3$

ⓑ $H + \frac{1}{2}O_2 \rightarrow H_2O$ ⓒ $N_2 + O_2 \rightleftharpoons 2NO$

Q Value of kp for a reacⁿ is 0.05 atm⁻¹. calculate the value of kc for the same reacⁿ at 727

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

$\begin{array}{r} 727 \\ 273 \\ \hline 1000 \end{array}$ $\begin{array}{r} 82 \\ \times 4 \\ \hline 328 \end{array}$

Solⁿ $k_p = k_c (RT)^{-1}$

$0.05 = k_c \left(\frac{0.0821 \times \cancel{1000}}{\cancel{1000}}\right)^{-1}$

$82\overline{)500}(0.08$

$\cancel{\frac{0.05}{82 \times 100}} = k_c$

$\begin{array}{r} 82.1 \\ \times 5 \\ \hline 410.5 \end{array}$

$0.05 \times 82.1 = k_c$

$\Rightarrow 4.105 = k_c$

Q. $A_{(s)} + B_{(g)} \rightleftharpoons 2C_{(g)}$

$\Delta n_g = 2 - 1 = 1$. At what temp does $\frac{k_p}{k_c}$ for the above reacⁿ is equal to 2

$\frac{k_p}{k_c} = (RT)^1$

$2 = RT$

$\frac{\cancel{2} \times 1000}{0.08\cancel{4}} 25 = T$

$25k = T$

Q $C_{(s)} + \frac{1}{2}O_{2}(g) \rightleftharpoons CO(g)$

$\Delta n = 1 - 1/2 = \frac{1}{2}$ Find the value of $\frac{kp}{kc}$

$\frac{kp}{kc} = (RT)^{1/2}$

Q For which reacⁿ $\frac{kp}{kc}$ value is maximum.

① $A_{(s)} + B_{(g)} \rightleftharpoons 2C_{(g)}$
(II) $3A_{(s)} + 2B_{(g)} \rightleftharpoons C_{(s)}$
(III) $5A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)}$
(IV) $A_{(s)} \rightleftharpoons B_{(g)} + 4C_{(g)}$ $\Delta n_g = 5 - 0 = 5$

$\left[\frac{kp}{kc} \rightarrow \text{max} \rightarrow \Delta n_g \rightarrow \text{max} \right]$

Q For which reacⁿ given reacⁿ $\log\left(\frac{kp}{kc}\right) + 2\log(RT) = 0$ is correct

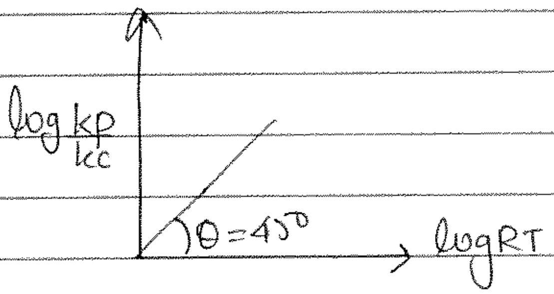
① $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
(II) $2SO_2 + O_2 \rightleftharpoons 2SO_3$
(III) $N_2 + 3H_2 \rightleftharpoons 2NH_3$
(IV) $2NaHCO_{3}(s) \rightleftharpoons Na_2CO_{3}(s) + CO_2(g) + H_2O(g)$

$\Delta n_g = 2 - 4 = -2$

$\frac{kp}{kc} = (RT)^{-2}$

$\log\left(\frac{kp}{kc}\right) = -2\log(RT)$. $\log\left(\frac{kp}{kc}\right) + 2\log(RT) = 0$.

Q log $\left(\frac{kp}{kc}\right)$ v/s log RT curve for the reac^n $A \rightleftharpoons nB$ is as given below. value of n



m = 1.

Sol^n $A \rightleftharpoons nB$

$A \rightleftharpoons 2B$ $\Delta ng = 2-1 = 1.$ $m = \Delta ng = $ slope.

1) 0
2) 1
[✓ 3) 2]
4) 3

$\log\left(\frac{kp}{kc}\right) = \log RT$

$y = mx$

$m = 1.$

Q. For a reac^n $A(s) + 2B(g) \rightleftharpoons \frac{3}{2} C(g)$. Value of kp is 3 times the value of kn. Calculate the total pressure

$$kp = kn(PT)^{\Delta ng}$$

$$\frac{3kn}{kn} = (PT)^{3/2 - 2} = -\frac{1}{2}$$

$$3 = (P_T)^{-1/2}$$

$$(3)^2 = PT^{-1}$$

$$PT = 1/9$$

⇒ FACTORS AFFECTING EQUILIBRIUM CONSTANT :-

① Mode of representation of reac$^{\underline{n}}$

$$A+B \rightleftharpoons C+D \; ; \; k$$

⇒ If reaction is reversed :-

$$C+D \rightleftharpoons A+B \; ; \; \left[k' = \frac{1}{k}\right]$$

② Stichometry of Reac$^{\underline{n}}$:-

$$A+B \rightleftharpoons C+D \; ; \; k$$

⇒ If a reaction is multiplied by n

$$nA+nB \rightleftharpoons nC+nD \; ; \; \left[k' = (k)^n\right]$$

③ If two or more than two reac$^{\underline{n}}$ are added to form a new reac$^{\underline{n}}$ then the equilibrium const of new reac$^{\underline{n}}$ is equal to the multiplication of the equilibrium const of the reac$^{\underline{n}}$ that were added.

$$A \rightleftharpoons C \; ; \; k_1$$
$$B \rightleftharpoons D \; ; \; k_2$$
$$A+B \rightleftharpoons C+D \quad k = k_1 \times k_2$$

eg

$$A \rightleftharpoons B \; ; \; k = 10$$
$$B \rightleftharpoons C \; ; \; k = 5$$
$$A \rightleftharpoons C \quad k'' = 50$$

$$C \rightleftharpoons A \quad k''' = 1/50$$

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IV. Temperature :-

$$\left[\begin{array}{ll} \text{ENDO ;} & K \propto T \\ \text{EXO ;} & K \propto \frac{1}{T} \end{array}\right]$$

Vant Hoff equation $\left[\log \frac{k_2}{k_1} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$

$$\log k_2 - \log_1 = \frac{\Delta H}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

- k_1 and k_2 equilibrium const of a reac^n at T_1 and T_2 temperature

ΔH = change in enthalpy

R = Gas const

→ 2cal $K^{-1} mol^{-1}$

→ $\boxed{8.314}$ Joule $K^{-1} mol^{-1}$

$\quad \| $

$\quad 25/3$

- T_1 and T_2 are initial & final temp in Kelvin

On increasing the Temp $(T_2 > T_1)$

Case I :- ENDOTHERMIC :-

$\Delta H = +ve$

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

$\therefore \log k_2 - \log k_1 > 0$

$\log k_2 > \log k_1$

$k_2 > k_1$. $\quad [T\uparrow \longrightarrow k\uparrow]$

Case IInd :- EXOTHERMIC REACN.

Temp increase

$\Delta H = -ve$

$\frac{T_2 - T_1}{T_1 T_2} = +ve$.

$\log k_2 - \log k_1 < 0$

$\log k_2 < \log k_1$

$\boxed{k_2 < k_1}$ $\boxed{T\uparrow \longrightarrow k\downarrow}$

⇒ Factors which not affect the Equilibrium const :-

① Pressure

② Volume of container

③ Catalyst

④ Addition of Inert gas

⑤ Initial concentration of Reactant & product.

Q. Consider a reac^n $H_2 + I_2 \rightleftharpoons 2HI$. If the value of equilibrium const for the above reac^n at 27°C is 160. Then what would be the value of equilibrium constant

① Volume of container is doubled

② Helium gas is added.

③ Pressure of system is doubled.

④ This reac^n is carried out in presence of catalyst which increase rate 10 times.

⑤ If reac^n is carried out with different initial concentration of H_2 & I_2

ol^n For (1 – V) ⟶ k = 60 {As k depend only on temp)

vi) If temp is raised to 127°c given $\Delta H_R = -27R$

$$\log\frac{k_2}{k_1} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$T_1 = 27 + 273 = 300$

$T_2 = 127 + 283 = 400$

$$\log\frac{k_2}{60} = \frac{-27R}{2.303R}\left(\frac{1}{300} - \frac{1}{400}\right)$$

$$\log\frac{k_2}{60} = \frac{-27}{2.303}\left(\frac{1\cancel{00}}{12\cancel{0000}}\right)$$

$$\log\frac{k_2}{60} = \frac{-27}{2.303 \times 12}$$

$$\log\left(\frac{k_2}{60}\right) = \frac{2\cancel{7} \cdot 10^{-2}}{\cancel{27}00}$$

take antilog both side

$$\text{Anti}\log\log\left(\frac{k_2}{60}\right) = \text{Antilog}(-0.01)$$

$$\text{Antilog}(x) = 10^x$$

$$\frac{k_2}{60} = \text{Antilog}(-0.01)$$

$$\left[k_2 = 60 \times 10^{-0.01}\right]$$

Q The partial pressure of PCl_3, Cl_2 & PCl_5 at equilibrium is 2atm, 4atm and 6atm respectively. Then what would be the partial pressure of PCl_5 at new equilibrium such that Partial pressure of PCl_3 and Cl_2 is doubled at new eq?

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$K_C = \frac{(P_{PCl_5})}{(P_{Cl_3})(P_{Cl_2})} = \frac{6}{2 \times 4} = \frac{3}{4}$$

$k_c = \frac{3}{4} = \frac{(P'_{Cl_5})}{(P'_{Cl_3})(P'_{Cl_2})}$

$\frac{3}{4} = \frac{(P'_{Cl_5})}{(4)(8)}$

$\frac{\cancel{4} \times 8 \times 3}{\cancel{4}} = (P'_{Cl_5})$

$24 = (P'_{Cl_5})$ (at new eq/librum)

Q Consider a reac^n $A(s) \rightleftharpoons 2B(g) + C(g)$

If equlibrium con^c of C is made upto 12 times then eq con^c of B would be:

Sol^n

$k_c = \frac{[C][B]^2}{\cancel{[A]}}$

Old New

$[A] = 1$

$[B] = 1 \longrightarrow x$

$[C] = 1 \longrightarrow 12$

$k_c = 1 \times 1$ (old equlibim)

$k_c = 1 = x^2 \times 12$ (old = new)

$\sqrt{\frac{1}{12}} = x \qquad \frac{1}{2\sqrt{3}} = x$

AIMPT Q

$Al(OH)_{3(s)} \rightleftharpoons Al^{3+}_{(aq)} + 3OH^-(aq)$

eq conc of OH$^-$ ions is increased upto 4 times. Then equlibrium conc of Al^{3+} would be.

K_c old $= 1 \qquad k_c = [OH^-]^3[Al^{3+}]$

$1 = [4]^3 \times x$

$\frac{1}{64} = x$

Q

T	500k	700k
k	1.1×10^{-9}	1.6×10^{-6}

T↑ K↑ (ENDO)

Q For an enothermic reacⁿ k_{c1} and k_{c2} are the equilibrium const at T_1 and T_2 temp respectivey. What woud be the relation b/w k_{c1} and k_{c2} on increasing the temp

(I) $k_{c1} = k_{c2}$
(II) $k_{c1} > k_{c2}$
(III) $k_{c1} < k_{c2}$
(IV) None

Exo

$K \propto \frac{1}{T}$ K↓ T↑

$k_{c1} > k_{c2}$

<u>Note</u>:- For thermoneutral reacⁿ $\Delta H = 0$ value of equilibrium const do not get changed upon changing the temperature.

Q. Value of equilibrium const for a reacⁿ is $N_2 + O_2 \rightarrow 2NO$; k_1
Find the equilibrium const of

① $2NO \rightarrow N_2 + O_2$ $k = \frac{1}{k'}$

② $\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightarrow NO$ $k = \sqrt{k_1}$

③ $NO \rightleftharpoons \frac{1}{2}N_2 + \frac{1}{2}O_2$ $k = \frac{1}{\sqrt{k_1}}$

④ $4NO \rightarrow 2N_2 + O_2$ $k = \frac{1}{(k_1)^2}$

① k_1 ; $N_2 + O_2 \rightleftharpoons 2NO$.

$$\Big\downarrow \text{rev}$$

$2NO \rightleftharpoons N_2 + O_2$ $\quad k = \frac{1}{k_1}$

Q. If the value of equilibrium const $2SO_2 + O_2 \rightleftharpoons 2SO_3$ is 156 then find the equilibrium const of $SO_3 \rightleftharpoons SO_2 + \frac{1}{2}O_2$

$$k_{eq} = \frac{1}{\sqrt{156}} = \frac{1}{12.5} = 8 \times 10^{-2}.$$

Q $N_2 + O_2 \rightleftharpoons 2NO$; k_1

Q $NOBr \rightleftharpoons NO + \frac{1}{2}Br_2$; k_2

Find the equilibrium const of $NOBr \rightleftharpoons \frac{1}{2}N_2 + \frac{1}{2}O_2 + \frac{1}{2}Br_2$.

$(ii) - \frac{1}{2}(i)$

$= NOBr \rightleftharpoons NO + \frac{1}{2}Br2$ $\quad k_{eq} = \frac{k2}{\sqrt{k_1}}$

$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftharpoons NO$

$NOBr \rightleftharpoons \frac{1}{2}N_2 + \frac{1}{2}O_2 + \frac{1}{2}Br_2$

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Q $N_2 + O_2 \rightleftharpoons 2NO ; k_1$

$NO_2 \rightleftharpoons NO + \frac{1}{2}O_2 ; k_2$

$NO_2 \rightleftharpoons \frac{1}{2}N_2 + O_2 ; k_3$.

Find the relation b/w $k_1 k_2$ and k_3.

(i) $k_3 = k_2 \times k_1^2$ Sol^n (II) $- \frac{1}{2}$ (I)

(ii) $k_3 = \frac{k_2}{k_1^2}$

$k_3 = \frac{k_2}{(k_1)^{1/2}} = \frac{k_2}{\sqrt{k_1}}$.

(iii) $k_3 = \sqrt{\frac{k_2}{k_1}}$

(iv) $k_3 = \frac{k_2}{\sqrt{k_1}}$

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Q

$N_2 + 3H_2 \rightleftharpoons 2NH_3 ; k_1$

$N_2 + O_2 \rightleftharpoons 2NO ; k_2$

$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O ; k_3$

Find the eqlibrm const of

$2NH_3 + \frac{5}{2}O_2 \rightleftharpoons 2NO + 3H_2O$

$-k_1 + k_2 + 3k_3 = -(I) + (II) + 3(III)$

$k_{eq} = \frac{k_2 (k_3)^3}{k_1}$

⇒ Application of Equilibrium const :-

① Stability of reactant & product

$$R \rightleftharpoons P$$

[Stability of product $\propto$ value of k]

$$\uparrow\uparrow K_{\downarrow\downarrow} = \frac{[P]\uparrow\uparrow_{\downarrow\downarrow}}{\uparrow\uparrow[R]\downarrow\downarrow}$$

$\left[\text{Stability of reactant } \propto \frac{1}{\text{value of } k}\right]$

k = equilibrium const

② Extend of reac^{n} or progress of reac^{n} :-

Case I $K > 10^3$.

- * Product will dominate over Reactant
- * $[P] >>> [R]$
- * Reaction almost goes to completion.

Case II $10^{-3} < k < 10^3$.

- * Both Reactant and product are in appreciable amount.

Case III $K < 10^{-3}$

- * $[R] >>> [P]$
- * Reactant dominates over product
- * Reaction hardly starts.

III. Direction of reaction :-

$$aA + bB \rightleftharpoons cD + dD$$

$$k_c = \frac{[C]_e^c [D]_e^d}{[A]_e^a [B]_e^b} \quad \text{(at equilibrium)}$$

$$\boxed{Q} = \frac{[D]_t^d [C]_t^c}{[B]_t^b [A]_t^a} \quad \text{(at any instance)}.$$

Reaction Quotient.

Case I: $Q = k$

equilibrium, no net direction.

Case II $Q < k$.

Reacⁿ moves in forward direcⁿ

Case III $Q > k$

Reacⁿ moves in backward direcⁿ.

Q Which product is more stable?

$A \rightleftharpoons B$; $k = 1.1 \times 10^{-19}$

$P \rightleftharpoons Q$; $k = 3 \times 10^{21}$

✓ $X \rightleftharpoons Y$ $k = 4 \times 10^{-11}$.

Y, Stability of product is directly proportional to k.

Q Which oxide is more stable ?

$MO \rightleftharpoons M + \frac{1}{2}O_2$; $k = 3.1 \times 10^{-19}$

$M_2O \rightleftharpoons 2M + \frac{1}{2}O_2$; $k = \cancel{3}4.4 \times 10^{-18}$

$M_3O_2 \rightleftharpoons 3M + O_2$; $k = 8 \times 10^{-33}$

Stability of oxide (Reactant) $\propto \frac{1}{k}$

→ Extend of Reaction :-

$A \rightleftharpoons B$; $k = 5 \times 10^{9}$

Which is correct at eq ?

(I) Product will dominate of reactant.
(II) Reactant will dominate over product.
(III) Reaction hardly start.
(IV) Both Ⓘ and Ⓘⓘⓘ

As $k \propto$ Product $[k > 10^3]$

Q $PCl_5 \rightleftharpoons PCl_3 + Cl_2$; $k_p = 2 \times 10^{-5}$ atm

At some instant of time, partial pressure of PCl_5 and PCl_3 and Cl_2 is 2×10^{-4} atm, 5×10^{-5} atm and 3×10^{-4} atm respectively. To achieve eq direction of reacⁿ

$$Q_P = \frac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})} = \frac{5 \times 10^{-5} \times 3 \times \cancel{10^{-4}}}{2 \times \cancel{10^{-4}}} = \frac{\overset{7.5}{\cancel{15}}}{\cancel{2}} \times 10^{-5}$$

$Q_P > k_P$ [Backward reacⁿ)

$Q_P = 7.5 \times 10^{-5}$

⇒ Degree of Dissociation :- (α)

It is the number of moles dissociated from 1 mole of reactant.

$$\alpha = \frac{\text{Dissociated moles}}{\text{Initial moles}}$$

$$A \rightleftharpoons nB$$

$t=0$ a mol

$t=t$ $a-x$. nx

a mol ⟶ x mol dissociated

1 mol ⟶ $\boxed{\frac{x}{a}\text{ mol}}$ dissociated

α

$0 \leq \alpha \leq 1$

$0 < \alpha < 1$ (in case of equilibrium) (As if $\alpha = 0$ (Reacⁿ doesn't start) if $\alpha = 1$ (Reacⁿ complete))

Eg:- 1. $2A \rightleftharpoons B$

initial moles $t=0$ $\boxed{a\,mol}$. 0

$t=eq$ $a-\boxed{2x}$ x .

⟶ dissociated moles

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

2. $3A \rightleftharpoons 2B + \frac{1}{2}C$.

$t=0$ $3a\,mol$ 0 0

t_{eq} $3a-3x$ $2x$ $\frac{1}{2}C$

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

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

$t=0$ $a\,mol$ $b\,mol$ 0 0

t_{eq} $(a-x)(b-2x)$ x $2x$

$\alpha_{total} = \frac{3x}{a+b}$

$\alpha_a = \frac{x}{a}$ $\alpha_b = \frac{2x}{b}$

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Q1 5 mol of 'A' were taken in a 2L Vessel. Upto equilibrium 2 mol of A got dissociated into B and C. Calculate.

1. Degree of dissociation of A
2. Conc^n of B at equilibrium

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

$$\alpha = \frac{\text{dissociated moles}}{\text{Initial moles}} = \frac{2}{5} = 0.4$$

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

(t=0)	5mol	0	0
(t=t)	5-2n	n	3C

$$5 - 2n = 3 .$$

$$2 = 2n$$

$$n = 1\ \text{mol} \qquad [B] = \frac{1}{2} = 0.5\ \text{mol}/L$$

Q2. 10 mol of PCl_5 were taken in a 2L vessel at 727°C. If degree of dissociation of PCl_5 is 40% or 0.4. Then calculate.

① Total moles at equilibrium
② kc
③ kp

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 .$$

$\alpha = 0.4 .$

(t=0)	10mol	0	0
	10-n	n	n
(tf)=	6	4	4

$$\frac{n}{10} = 0.4$$

$$n = 4$$

① Total moles at equilibrium = 14 moles

$$② \quad kc = \frac{\left(\frac{4}{2}\right)\left(\frac{4}{2}\right)}{\left(6/2\right)} = \frac{2 \times 2}{3} = \left(\frac{4}{3}\right) M$$

$$③ \quad kp = kc\,(RT)^{\Delta n}$$

$$= \frac{4}{3}\left(\frac{10\cancel{00} \times 0.0821}{\cancel{100}}\right)^{1}$$

$$= \frac{4}{3} \times 80$$

$$= 1\,\frac{320}{3}$$

$$= 106.6\ \text{atm}$$

Q3. 4 mol of AB_2 was taken in a vessel such that 40% of AB_2 dissociate into AB and B_2. If total pressure at equilibrium is P then calculate :-

① Dissociated moles

② Kp

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

t=0	4	0	0
(t=t)	(4-2x)	(2x)	(x)
(t=t)	(4-1.6)	(1.6)	(0.8)
	=2.4	1.6	0.8

$\alpha = 0.4$

$0.4 = \frac{2x}{4}$

$0.4 \times 2 = 2x$

$x = 0.8$.

1
1.6
0.8
2.4
4.8

① Dissociated moles = 0.8×2
= 1.6 moles.

② $$kp = \frac{(P_{AB})^2 (P_{B_2})}{(P(AB_2))^2} = \frac{\left(P\times\frac{1.60}{4.8}\right)^2\left(P\times\frac{0.8}{4.8}\right)}{\left(P\,\frac{2.4}{4.8}\right)^2}$$

$$\frac{\left(\frac{P}{3}\right)^2\left(\frac{P}{6}\right)}{\left(\frac{P}{2}\right)^2} \qquad \frac{\cancel{P^2}\times P \times \overset{2}{\cancel{4}}}{(9\times\underset{3}{\cancel{6}})\times\cancel{P^2}}$$

$$kp = \frac{2P}{27} \text{ atm}$$

Note :-

* For reaction having $\Delta n_g = 0$ kp and kc can be directey calculated from moles also.

Q. 4 mole each of H_2 and I_2 are allowed to mix in a 10L vessel to form 2 mole of HI. Calculate the value of kp

$$H_2 + I_2 \rightleftharpoons 2HI$$

(t=0) 4mol 4mol 0

(t=teq) $4-x$ $4-x$ $2x$

$=3$ 3 2

Since $\Delta n_g = 0$ so calculate from moles

$2x = 2$

$x = 1$

$$kp = \frac{2\times2}{3\times3} = \frac{4}{9} = \frac{(n_{HI})^2}{(n_{H_2})(n_{I_2})}$$

Q 4 mole of 'A' and 4 mole of 'B' are mixed together in a 10L vessel to form 'C and D' A/c to reaction. If value of equilibrium const for a reacⁿ is '4'. Then calculate the conⁿ of B at equilibrium

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

(t=0) 4 4

(t=t) $(4-x)$ $(4-x)$ (x) (x)

$$kc = \frac{x^2}{(4-x)^2} \qquad 4 = \left(\frac{x}{4-x}\right)^2$$

$\frac{x}{4-x} = 2$. $x = 2(4-x)$

$x = 8 - 2x$.

$3x = 8$ $x = 8/3$.

conc of $B = 4 - 8/3$

$= \frac{12-8}{3} = 4/3\times10 = \frac{4}{30}$ M

Q. Initially '1' mole each of 'A', 'B', 'C' were taken in a '1 L' vessel which is correct at equilibrium :-

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

(1) $[A] = [B] = [C]$

(2) $[A] = [B]$ is more than 1.

(3) $[C] < [D]$

✓(iv) $[D] < 1$

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

$(t=0)$ 1 1 1

$(t=t_{eq})$ $(1-x)$ $(1-x)$ $(1+x)$ (x)

$[A] = [B]$ $[C] > 1$

$[D] < 1$

$n_A > 0$

$1 - x > 0$

$1 > x$ or $x < 1$

$[D] = x < 1$

Q. Initially SO_3 gas was present at 200 mm of Hg. At equilibrium Tp of mixture was found to 250 mm Hg. Calculate the value of kp for the reaction

$$2SO_3 \rightleftharpoons 2SO_2 + O_2$$

$(t=0)$ $\underline{200\text{ atm}}$ 0 0

dissociated pressure

$(t=t)$ $(200 - \boxed{2x})$ $(2x)$ (x)

$= 100$ 100 50

$Tp = 200 - \cancel{2x} + \cancel{2x} + x$

$250 = 200 + x$

$x = 50$.

$$kp = \frac{(50)\cancel{(100)}^2}{\cancel{(100)}^2} = 50 \text{ ~~atm~~ mm Hg}$$

✓ $\left[\alpha = \frac{2x}{200} = \frac{\text{Dissociated pressure}}{\text{Initial pressure}}\right] =$

Q At 60° & 2atm , N_2O_4 is 50% dissociated into NO_2 as:
$N_2O_4 \rightleftharpoons 2NO_2$

Calculate kp ?

$N_2O_4 \rightleftharpoons 2NO_2$ $\alpha = 0.5$

(t=0) 2atm

(t=t) $(2-x)$ $2x$ $\alpha = \frac{x}{2}$

$2-1$ 2 $1 = x$

$= 1$ 2

$kp = \frac{(2)^2}{(1)} = 4$ atm

Q 200g $CaCO_3$ is 50% dissociated into CaO and CO_2 At 727°C. Calculate the value of kp. Volume of container 10L

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

(t=0) · $\frac{\cancel{200}\ 2}{\cancel{100}}$ 0 0 $\alpha = 0.5$

$2-x$ x x $x = 1$

1 1 1.

$kc = \frac{(\cancel{1})}{10} \times \frac{1}{10} = \frac{\cancel{1}}{100}$

$kc = (CO_2)$
$= \frac{1}{10}$

~~$kp = kc(RT)^{\Delta n}$~~
~~$= \frac{1}{100}(R \times 1000)^2$~~
~~$kp = R^2 \times \frac{1000 \times 1000}{100}$~~

$R^2 \times 10000$
$= R^2 \times 10^4$ atm

$kp = \frac{1}{10} \times (R \times 1000)$
$= 100R$ atm

2/ $NH_4COONH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$. If Tp at equilibrium = 1·2 atm Then calculate the value of kp.

$$NH_4COONH_2(s) \rightleftharpoons 2NH_{3(g)} + CO_2(g)$$

$$\begin{array}{llll} t=0 & 1\text{ mol} & 0 & 0 \\ t_{eq} & (1-x) & 2x & x \end{array}$$

$$Kp = (P_{NH_3})^2 (P_{CO_2})^1$$

* In total mole solid is neglected

$P_{NH_3} = Tp \times \chi_{NH_3}$

$= 1.2 \times \frac{2\cancel{x}}{3\cancel{x}} = \frac{\overset{4}{\cancel{12}}}{10} \times \frac{2}{\cancel{3}} = 0.8$

$P_{CO_2} = Tp \times \frac{x}{3x} = 1.2 \times \frac{1}{3} = 0.4$

$$\begin{array}{r} \scriptstyle 1 \\ 64 \\ \times 4 \\ \hline 256 \end{array}$$

$kp = (0.8)^2 (0.4)$

$= \frac{08 \times 08 \times 04}{1000} = \frac{256}{1000} = 0.256 \text{ atm}^3$

Q. 'A' and 'B' are both present initially at 0.5 M. When equilibrium is achived conc. of D at equilibrium is found to be 0.2 M. Calculate the value of kc ?

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

$(t=0)$ 0.5 M 0.5 M

$(0.5-x)$ $(0.5-x)$ (x) $(2x)$

$(t = t_{eq})$ 0.4 (0.4) (0.1) (0.2)

$0.2M = 2x$

$x = 0.1$

$$k_c = \frac{(0.2)^2(0.1)}{0.4 \times 0.4} = \frac{0.\cancel{2} \times 0.\cancel{2} \times 0.1}{\underset{2}{\cancel{0.4}} \times \underset{2}{\cancel{0.4}} \times 1} \times 10$$

$$= \frac{0.25}{10} = 0.025\ M$$

Q H₂ and I₂ are allowed to react in a 10 L vessel to form HI. If the equilibrium concentration of H_2, I_2 and HI is found to be 2.4 M, 1.6 M and 1.2 M respectively. Then calculate ① kc ⑪ kp ⑪⑪ Initial conc.ⁿ of H_2 and I_2

$$H_2 + I_2 \rightleftharpoons 2HI$$

(t_{eq}) 2.4 1.6 1.2

① $$k_c = \frac{(1.2)^2}{2.4 \times 1.6} = \frac{1.\cancel{2} \times 1.\cancel{2}\ 6}{\underset{2}{\cancel{2.4}} \times \cancel{1.6}\ 8} = 3/8$$

⑪ . $k_c = k_p$ (As $\Delta n_g = 0$)

$k_p = 3/8$

⑪⑪ $$H_2 + I_2 \rightleftharpoons 2HI$$

a b

(t_{eq}) $a-x$ $b-x$ $2x$

$2x = 1.2$ $x = 0.6$

$b = 2.2$

$b - 0.6 = 1.6$

$a = 3$

$a - 0.6 = 2.4$

* For P and T = const

$V \propto n$

$\boxed{V\% = n\%}$

Volume percent = mole percent

= mole fraction percent . = x percent

mole percent = $\left(\frac{n_m}{n_T}\right) \times 100$

Q. At certain temp and 10^5 Pa Iodine vapour found to contain 60% Iodine atom by volume. Calculate kp?

$$I_2 \rightleftharpoons 2I(g).$$

Sol^n

Volume % $(I(g)) = 60$

mole % $(I(g)) = 60$

$X_I = \frac{60}{100} = 0.6$.

$X_{I_2} = 0.4$

$P_I = 0.6 \times 10^5$

$P_{I_2} = 0.4 \times 10^5$

$$kp = \frac{(P_I)^2}{(P(I_2))} = \frac{(0.6 \times 10^5)^2}{0.4 \times 10^5}$$

$$= \frac{0.\overset{3}{\cancel{6}} \times 0.6\overset{3}{\cancel{6}}}{0.\cancel{4}\,\cancel{2} \times 10} \times \frac{10^{10}}{10^5}$$

$$= 9 \times 10^{5-1} = 9 \times 10^4 \text{ atm}$$

Note :- When initial information of reactant is not given then stichometric coefficient of reactant can be treated as initial moles.

eg. $2A \rightleftharpoons B + C$ Given values :- α and P_T

$t=0$ 2 mol   0   0

t_{eq} $2-2x$ x x

$\alpha = \frac{2x}{2} = x$ $t = t_{eq}$ $2-2\alpha$ α α ✓

(alway $\alpha = x$)

Q. Degree of dissociation of PCl_5 is α and total pressure at eqlm is 'P'. Then find kp, find α in terms of kp and 'p'

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$t=0$ 1   0   0

$(t = t_{eq})$ $1-x$ x x

$(t = t_{eq})$ $(1-\alpha)$ (α) (α)

$X_{Cl_2} = \frac{\alpha}{1+\alpha}$

$P_{Cl_2} = P\left(\frac{\alpha}{1+\alpha}\right)$

Total moles $= (1+\alpha)$.

$$kp = \frac{\left(\frac{P\alpha}{1+\alpha}\right)\left(\frac{P\alpha}{1+\alpha}\right)}{\left(\frac{P(1-\alpha)}{1+\alpha}\right)} = \frac{P^2\alpha^2}{(1+\alpha)^{\cancel{2}}\,\frac{(1-\alpha)\times P}{\cancel{(1+\alpha)}}}$$

$$\left[kp = \frac{P\alpha^2}{(1-\alpha^2)}\right]$$

$kp(1-\alpha^2) = P\alpha^2$

$kp - kp\alpha^2 = P\alpha^2$

$kp = \alpha^2(kp + P)$

$$\left[\alpha = \sqrt{\frac{kp}{kp+P}}\right]$$

Learn value of these two reacⁿ (or same-format reacⁿ):-

① $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

x $k_p = \frac{\alpha^2 P}{1-\alpha^2}$

② $N_2O_4 \rightleftharpoons 2NO_2$

$k_p = \frac{4\alpha^2 P}{1-\alpha^2}$.

Q If degree of dissociation (α) of AB_2 is 50% and total pressure at equlib is 15 atm. Calculate kp.

$2AB_2 \rightleftharpoons 2AB + B_2$.

		$2AB_2$	$2AB$	B_2
	$(t=0)$	2	0	0
	(t_{eq})	$2-2x$	$2x$	x
$\alpha = \frac{2x}{2}$	(t_{eq})	$2-1$	2×0.5	0.5
$\alpha = x$		$=1$	1	0.5

Total moles $= 2.5$

$x = 0.5$

$$k_p = \frac{\left(\frac{15\times0.5}{2.5}\right)\cancel{\left(\frac{15\times1}{2.5}\right)^2}}{\cancel{\left(\frac{15\times1}{2.5}\right)^2}} = \frac{15\times1}{5}$$

$= 3$ atm

$$k_p = \frac{(P_{B_2})(P_{AB})^2}{(P_{AB_2})^2}$$

Q. If the eqlibrium const of Reac^{n} P

$A \rightleftharpoons B + C$; kp1 $\qquad kp1 = \frac{\alpha^2 P_1}{1-\alpha^2}$

$X \rightleftharpoons 2Y$; kp2 $\qquad kp^2 = \frac{4\alpha^2 P_2}{1-\alpha2}$

If ratio of total pressure at equilibrium in both reac^{n} is $\left(\frac{20}{3}\right)$ and degree of dissociation of A and X is equal then calculate the ratio of $\frac{kp1}{kp2}$.

Sol^{n} $\quad \frac{kp1}{kp2} = \frac{\alpha^2 P_1}{1-\alpha^2} \times \frac{1-\alpha^2}{4\alpha^2 P_2}$

$\frac{kp1}{kp2} = \left(\frac{20}{3}\right)\frac{1}{4} = 5/3$.

Q. 1 mol of H_2 gas is present in a 1L vessel and 3 mol of I_2 gas is present in a 3L vessel. When equibrium is attained con^{c} of HI was found to be 0.2M. Calculate

① kc

(ii) con^{c} of $[H_2]e$ $[I_2]e$.

$H_2 + I_2 \rightleftharpoons 2HI$. $\qquad$ Total volume = 4L

(t=0) $\quad \frac{1}{4}M \quad \frac{3}{4}M \quad 0$

(teq) $\quad \left(\frac{1}{4}-x\right) \quad \left(\frac{3}{4}-x\right) \quad \frac{2x}{\cancel{4}}$

(teq)

~~$\frac{2x}{4} = 0.2$~~ $\qquad 2x = 0.2$

$x = 0.4$ $\qquad x = 0.1$

~~(0.25 − 0.1)~~ $\left(\frac{3}{4} - 0.1\right)$

$$H_2 + I_2 \rightleftharpoons 2HI$$

$$t=0 \quad 1 \quad 3$$

$$(t=t) \quad (1-x) \quad (3-x) \quad 2x$$

$$= 0.6 \quad 2.6 \quad 0.8$$

$$2x = 0.2 \times 4$$

$$x = 0.4$$

$$kc = \frac{\left(\frac{0.8}{4}\right)^2}{\left(\frac{0.6}{4}\right)\left(\frac{2.6}{\cancel{4}}\right)} = \frac{0.8 \times 0.8}{0.6 \times 2.6} \; 4 \; 4$$

$$= \frac{\cancel{8} \times \cancel{8}}{{}_3\cancel{6} \times \cancel{26}\,13}$$

$$\frac{[H_2]e}{[H_2]e} = \frac{\frac{2.6}{4}}{\frac{0.6}{4}} = \frac{2.6}{0.6} = \frac{\overset{13}{\cancel{26}}}{\cancel{6}\,3} = \frac{13}{3}$$

$$\left[k_c = \frac{16}{39}\right]$$

⇒ Le-chatelier's principle :-

Factors.	Equilibrium const	Equilibrium.
concⁿ	×	✓
P	×	✓
V	×	✓
Inet Gas	×	✓
Temp	✓	✓
Catalyst	×	×

According to the principle if a system at equilibrium is subject to change in any of the factors like concentration, pressure temp, etc. Then equilibrium will get disturbed and equilibrium will shift in that direction in which the effect of that factor get nullify or cancelled out.

⇒ Effect of concentration :-

* If a substance is added then equilibrium will shift in that direction in which that added substance is consumed.

* If a substance is removed then equilibrium will shift in that direction in which that removed substance is formed.

Note :- Change in concⁿ of solid and liquid do not affect equilibrium

II) Effect of volume :-

$\Delta n_g = 0$: no effect on equilibrium

$\Delta n_g \neq 0$: On increasing the volume equilibrium will shift towards more number of moles & vice versa.

$A \rightleftharpoons 2B$

$r_f = r_b$

$r_f\downarrow = k_f[A]\downarrow$

$r_{b\downarrow\downarrow} = k_b[B]^2\downarrow$

$V\uparrow \quad [A]\downarrow$

$[B]\downarrow\downarrow$

$r_f \neq r_b$

$r_f > r_b$ → Forward

$A \rightleftharpoons B$

$r_f = r_b$

$r_{f\downarrow} = k_f[A]\downarrow$

$r_{b\downarrow} = k_b[B]\downarrow$

$V\uparrow \quad [A]\downarrow$

$[B]\downarrow$

$r_f = r_b$

(Hence no effect).

III) Effect of pressure :-

$\Delta n_g = 0$: no effect on equilibrium

$\Delta n_g \neq 0$: On increasing pressure equilibrium will shift towards less number of moles & vice versa.

$P\uparrow = V\downarrow = \frac{n}{V}\uparrow \Rightarrow$ equilibrium will shift towards less moles

(IV) Temperature :-

Both equilibrium and equilibrium const get affected by temperature.

* Case 1 :- Endothermic reac^n :-

$$A + \text{Heat} \underset{\text{Heat produced}}{\overset{\text{Heat consumed}}{\rightleftharpoons}} B$$

Endothermic direction

Exothermic direction

On increasing the temp equilibrium will shift in forward direction and vice versa

* Case 2 :- Exothermic reac^n :-

$$A \underset{\text{Heat consumed}}{\overset{\text{Heat produced}}{\rightleftharpoons}} B + \text{Heat}$$

Exothermic direction

Endothermic direction

On increasing the temp equilibrium shifts in backward direction and vice versa.

ENDOTHERMIC	EXOTHERMIC.
$K \propto T$	$K \propto \frac{1}{T}$
$T\uparrow\ K\uparrow \Rightarrow$ Forward.	$T\uparrow \Rightarrow K\downarrow =$ Backward
$T\downarrow\ K\downarrow \Rightarrow$ Backward	$T\downarrow \Rightarrow K\uparrow =$ Forward,

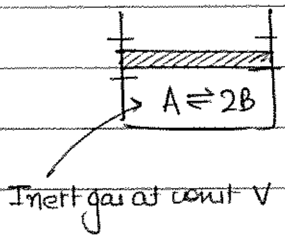
* $K\uparrow \Rightarrow$ Forward
$K\downarrow \Rightarrow$ Backward. ↙ Specific for Temperature.

Ⓥ Effect of addition of Inert gas :-

ⓐ Inert gas at const. volume :-

→ No effect on equilibrium .

Partial pressure and concentration of reacting species di remains const on addition of Inert gas at const. volume, thus equilibrium doesn't get disturbed.



$$P\textcircled{V} = n\textcircled{RT}$$

$$\frac{P_T}{n_T} = \frac{RT}{V} = \text{const}$$

$$r_f = r_b$$

$$r_f = k_f[A] \quad \begin{cases} r_f = k_f[A] \\ r_f = k_f(P_A) \end{cases}$$

$$r_b = k_b[B]^2 \quad \begin{cases} r_b = k_b[B]^2 \\ r_b = k_b(P_B)^2 \end{cases}$$

$$\left.\begin{aligned} [A] &= \frac{n_A}{V} \\ [B] &= \frac{n_A}{V} \end{aligned}\right\} \text{no change}$$

$$\underset{\text{const}}{\underline{P_A}} = P_T n_A = \overset{= \text{const}}{\frac{P_T\uparrow n_A}{n_T\uparrow}}$$

ⓑ Inert gas at const pressure :-

$\Delta n_g = 0$; no effect on equilibrium

$\Delta n_g \neq 0$. on adding inert gas at const pressure, volume get increased thus equilibrium will shift towards more number of moles.

(VI) Effect of catalyst → NO Effect.

Q. $\overbrace{Pcl_5}^{1mole} \rightleftharpoons \overbrace{Pcl_3 + cl_2}^{2mole}$

What would happen if

(I) Helium gas is added at const volume = No effect
(II) Helium gas is added at const pressure = Forward
(III) Cl_2 gas is added keeping volume const = Backward.
(IV) Substance is added which consume Pcl_3 = ~~B~~ Forward
(V) Compress the equilibrium mixture. = Backward.

Q. $\overbrace{CaCO_3(s)}^{0\ mole} \rightleftharpoons \overbrace{CaO_{(s)} + CO_{2(g)}}^{1\ mole}$ $\Delta H = +ve$.

Which will shift the equilibrium in reverse direction?
(I) addition of CaO × (solid)
(II) decreasing the pressure ×
(III) Increasing the temp × $T\uparrow$ = ENDO $\rightarrow k\uparrow$ $k \propto T \Rightarrow$ Forward
(IV) decreasing the temp.

$$T\downarrow \Rightarrow K\downarrow$$
$$\Downarrow$$
Backward

Q. $\overbrace{N_2 + O_2}^{2mole} \rightleftharpoons \overbrace{2NO}^{2mole}$; $\Delta H = +ve$

Which will shift the equilibrium towards right?
(I) Increase the P
(II) increase the V
(III) Increase the temp $T\uparrow K\uparrow$ = Forward.
(IV) Add NO

$\Delta n_g = 0$ P, V = no effect
add NO = Backward.

Q What are the favourable condition for formation of Amonia .

$$\overbrace{N_2 + 3H_2}^{4\text{mole}} \rightleftharpoons \overbrace{2NH_3}^{2\text{mole}} , \quad \Delta H = -ve$$

1. Add N_2 and H_2
2. Remove NH_3
3. $T \propto \frac{1}{k}$ T↓ K↑ = Forward
4. Pressure ↑ = Forward
5. Volume ↓ = Forward .
6. Addⁿ of inert gas at const pressure V↑ = Backward (X)

Q $$\overbrace{2SO_3}^{2\text{mole}} \rightleftharpoons \overbrace{2SO_2 + O_2}^{3\text{mole}} \quad \Delta H = +ve .$$

Condition for minimum SO_3 .

SO_3 — ~~rem~~ add

SO_2, O_2 = remove

P↓

V↑

K↑ T↑

Q $$\overbrace{A}^{1\text{mole}} \rightleftharpoons \overbrace{2B + C}^{3\text{mole}} ; \quad \Delta H = +ve$$

Which condition is correct for minimum yield of C

Ar. (1) 500°C , 1 atm

(2) 50°C , 1 atm

[✓ (3) 50°C , 50 atm .] K↓ T↓ P↑ = Backward .

(4) 500°C , 50 atm .

Q. $\overleftarrow{aA + bB \rightleftharpoons cC + dD}$

High pressure ($P\uparrow$) and Low temp ($T\downarrow$) are favourable condition for the equilibrium to shift in backward direction. Which is correct.

Soln

$(a+b) < (c+d)$ $\Delta H = +ve$

High P ⟶ less moles $T\downarrow\ k\downarrow$ (ENDOTHERMIC)

Q $\overleftarrow{aA \rightleftharpoons bB}$

High V, backward.

$V\uparrow\ n\uparrow \Rightarrow a > b$

Q $kp < kc$ High pressure ⟶ less moles

$\frac{kp}{kc} < 1$ $\Delta ng = -ve$ ↓

$\overrightarrow{\text{more moles} \rightleftharpoons \text{less more}}$

So eqlibrium shift in forward direction.

Q. $A \rightleftharpoons 2B + 3C$ } Same conditional

$E + C \rightleftharpoons F$

If F is removed, then conc of A & B will ?

Soln 2nd reaction eqlm disturbed ⟶ Forward direction

So C↓ decreases so 1st reaction ⟶ Forward direction to increas
the [C] ↑ so [A]↓ and [B]↑

⇒ Relation b/w 'α' and pressure or volume :-

$$\alpha \propto (V)^{\frac{\Delta ng}{np}}$$

$$\alpha \propto \left(\frac{1}{P}\right)^{\frac{\Delta ng}{np}}$$

α = degree of dissociation
V = container's volume
P = total pressure at eq/lm
Δng = (Sum of stichometric coefficient of gase product) − (Sum of stichometric coefficient of gases reactant)
np = sum of stichometric coeffient of gases product

eg:- $N_2O_4 \rightleftharpoons 2NO_2$

$\Delta ng = 2-1 = 1$

$np = 2$ $\alpha \propto (V)^{\frac{\Delta ng}{np}} \propto (V)^{\frac{1}{2}} = \sqrt{v}$

If reac^n shift :-
Forward ⇒ α↑
Backward ⇒ α↓

Q (i) $2HI \rightleftharpoons H_2 + I_2$ (ii) $2NH_3 \rightleftharpoons N_2 + 3H_2$

What would happen to degree of dissociation

A/S (i) P is (↑) $\Delta ng = 0$ α = no change
(ii) V ↑ $\Delta ng = 0$ α = no change
(iii) T↑ (Endothermic) k↑ → Forward α↑
(iv) IG is added at const V → no change
(v) IG is added at const P → V(↑) $\Delta ng = 0$ ⇒ no change

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(ii) (i) P ↑ $\Delta n_g = 4-2 = 2$

$\alpha \propto \left(\frac{1}{P}\right)^{\frac{2}{4}} \quad \left(\frac{1}{P}\right)^{1/2} \quad \alpha \downarrow$

(ii) V ↑ $\Delta n_g = 2 \quad \alpha \propto (V)^{2/4} \quad (V)^{1/2} \quad \alpha \uparrow$

(iii) T ↑ Endothermic K ↑ → Forward ⇒ α ↑

(iv) IG const volume = no change

(v) IG const pressure → V(↑) ⇒ forward ⇒ α(↑)

Q $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ $\quad \Delta n_g = 2-1 = 1$, $n_p = 2$

If volume of container is made 8 times then degree of dissociation would be

$$\alpha \propto (V)^{\frac{\Delta n_g}{n_p}} \quad \alpha (V)^{\frac{1}{2}} \quad \alpha\ (8V)^{1/2}$$

$$= 2\sqrt{2}(V)^{1/2}$$

α increases to $2\sqrt{2}$ times

Q $2NH_3 \rightleftharpoons N_2 + 3H_2$ $\quad \Delta n_g = 2$, $n_p = 4$

If degree of dissociation of NH_3 at total pressure P_1 & P_2 is 1% & 2% respectively calculate $\frac{P_1}{P_2}$

$$\frac{\alpha_1}{\alpha_2} = \frac{\left(\frac{1}{P_1}\right)^{\frac{2}{4}}}{\left(\frac{1}{P_2}\right)^{2/4}} \quad \frac{\left(\frac{1}{P_1}\right)^{1/2}}{\left(\frac{1}{P_2}\right)^{1/2}} \quad = \left(\frac{1}{2}\right)^2 = \left(\frac{P_2}{P_1}\right)$$

$$\frac{P_1}{P_2} = 4:1$$

⇒ Relation b/w 'α' and Vapourdensity (V.D) :-

$$n_1 A \rightleftharpoons n_2 B + n_3 C$$

$$\boxed{\begin{aligned} \alpha &= \frac{n_1}{\Delta n}\left(\frac{D_T - D_0}{D_0}\right) \\ \alpha &= \frac{n_1}{\Delta n}\left(\frac{M_T - M_0}{M_0}\right) \end{aligned}}$$

Δn_g = Sum of stichomery product − sum of stichomery Reacatant.

$$= (n_3 + n_2) - (n_1)$$

n_1 = Sum of stichometric coefficient of reactant.

D_T/M_T = Theoritical vapour density / Theoritical molar mass.

D_0/M_0 = Observed vapour density / Observed molar mass

$$\boxed{D_T = \frac{M_T}{2}, \quad D_0 = \frac{M_0}{2}.}$$

Q If vapour density of NH_3 when dissociated is 5 then calculate α

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

$n_1 = 2$

$\Delta n = 2$

$$D_T = \frac{Mwt}{2} = \frac{17}{2} \qquad D_0 = 5$$

$$\alpha = \frac{2}{2}\left(\frac{\frac{17}{2} - 5}{5}\right) = 1\left(\frac{17 - 10}{10}\right) = \frac{7}{10} = 0.7$$

$\alpha = 0.7$. or 70%

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Q. If degree of dissociation of SO_3 is 40%. Then calculate the value of $\left(\frac{D}{d} = \frac{D_T}{D_0}\right)$ Calculate the slope

$$2SO_3 \rightleftharpoons 2SO_2 + O_2$$

$\Delta n = 1$

$n_1 = 2$

$$\alpha = \frac{n_1}{\Delta n}\left(\frac{D_T - D_0}{D_0}\right)$$

$$0.4 = \frac{1}{2}\left(\frac{D_T - D_0}{D_0}\right)$$

$0.8 D_0 = D_T - D_0$

$1.8 D_0 = D_T$

$\cancel{\frac{D_T}{D_0} = \frac{1 \times 10}{1.8} = \frac{5}{9}}$

$0.2 D_0 = D_T - D_0$

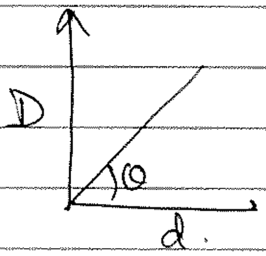
$1.2 D_0 = D_T$

$\cancel{\frac{D_T}{D_0} = \frac{1 \times 10}{1.2}\ \frac{6}{6}}$

$\frac{D_T}{D_0} = 1.2$

$\frac{6}{5}$

Q.



$$m = \tan\theta = D/d = 5/6 = \frac{1}{1.2}$$

Q If degree of dissociation of N_2O_4 at 1 atm 27°C is 20% Calculate the following
(1) Observed V.D
(2) Observed Molar mass
(3) ρ of eqlm mixture.

$$N_2O_4 \rightleftharpoons 2NO_2$$

$n_1 = 1$

$\Delta n = 2 - 1 = 1$

$$D_T = \frac{28 + 64}{2} = \frac{\cancel{92}}{\cancel{2}}\,46$$

$$\alpha = \frac{n_1}{\Delta n}\left(\frac{D_T - D_0}{D_0}\right)$$

$$\alpha = 1\left(\frac{46 - D_0}{D_0}\right)$$

$0.2 D_0 + D_0 = 46$

$$D_0 = \frac{\overset{23}{\cancel{46}} \times \overset{5}{\cancel{10}}}{\cancel{12}\ \cancel{6}\ 3} = \frac{115}{3}$$

$$\begin{array}{r} 1 \\ 23 \\ \times 5 \\ \hline 115 \end{array}$$

$2 \times VD = M_{observed}$

$\frac{2 \times 115}{3} = \frac{230}{3} = M_O = 76.6$

ii) ρ of eq/lm mixture $PV = nRT$

$1N_2O_4 \rightleftharpoons 2NO_2$
$1 \qquad 0$
$(1-x) \qquad 2x$.

$\alpha = \frac{x}{1}$ $1-0.2 \qquad 2\times0.2$
$0.8 \qquad 0.4$

$n_T = 1.2$

$V = \frac{1.2 \times R \times 30\cancel{0}}{1\cancel{0}}$
$= 360R$.

$\rho = \frac{\text{Molarmass}}{\text{volume}}$

$\rho = \frac{76.6}{360R} = 8.1\ gm/L$

⇒ PHYSICAL EQUILIBRIUM :-

The equilibrium exist b/w the different states of a particular substance is known as physical equilibrium, which is Dynamic in nature.

eg. $H_2O(l) \rightleftharpoons H_2O(g)$

✗✱ On increasing the pressure equilibrium shifts towards less volume
* Order of volume :-

$V_{solid} < V_{liquid} < V_{gas}$ (In general)

But in case of H_2O :-

$V_{H_2O(l)} < V_{H_2O(s)} < V_{H_2O(g)}$.

* Solid – Liquid Equilibrium :-

$X(s) \rightleftharpoons X(l)$ $\Delta H = +ve$ $(T \propto k \quad T\uparrow k\uparrow)$

less volume more volume

- * On increasing the temp, equilibrium will shift in forward direction
- * On increasing the pressure, equilibrium will shift in backward direction

$H_2O(s) \rightleftharpoons H_2O(l)$; $\Delta H = +ve$.

More volume less volume.

* On increasing the pressure, equilibrium will shift in Forward direction

(a) more ice melts or more liquid is formed.

(b) melting point decreases

* Liquid – Gas Equilibrium

$H_2O(l) \rightleftharpoons H_2O(g)$ $\Delta H = +ve$.

less volume more volume.

* On increasing the temp equilibrium will shift in Forward direction

* On increasing the pressure, equilibrium shift in Backward direction

(a) more liquid is formed

(b) Boiling point increase.

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⇒ IONIC EQUILIBRIUM :-

Some basic points :-

① $N = \text{Molarity} \times \text{valency factor}$.

② no of moles = $M \times V_L$

no of moles = $\frac{M \times V_{(mL)}}{1000}$

milli moles = $M \times V_{ml}$.

③ no of equivalents = $N \times V_L$

no of equivalent = $\frac{N \times V_{ml}}{1000}$.

Melliequivalent = $N \times V_{ml}$

④ no of equivalents = Moles × valency factor.

⑤ **Electrolytes :-**

ⓐ Strong electrolyte

- * completely ionised.
- * $\alpha = 1$ or 100%
(degree of ionisation)
- * Strong acid, strong ~~weak~~ base, salt.

Strong acid :- $HClO_4$, HI, HBr, H_2SO_4, HCl, HNO_3

Strong base :- NaOH, KOH, RbOH, CsOH, $Ba(OH)_2$

Salt :- $\overset{+}{Na}\overset{-}{Cl}$, CH_3COONa, NH_4Cl, Na_2SO_4.

ⓑ weak electrolyte.

- * partially ionised.
- * $\alpha < 1$ or $\alpha < 100\%$

eg : weak acid & weak base

Weak acid :- CH_3COOH, HCN, HCOOH, H_2CO_3, H_2S, H_3PO_4, H_3PO_3, H_3PO_2, HClO, $HClO_2$, $HClO_3$, HNO_2, etc.

Weak base :- NH_4OH, $Zn(OH)_2$, $Fe(OH)_3$, $Cu(OH)_2$, $Al(OH)_3$, etc

⑥ Logarithm :-

$\log(a\times b) = \log a + \log b$

$\log\left(\frac{a}{b}\right) = \log a - \log b$

$\log a^{n} = n\log a$.

$\log 1 = 0$

$\log 2 = 0.3$

$\log 3 = 0.48$

$\log 4 = 0.6$

$\log 5 = 0.7$

$\log 6 = 0.78$

$\log 7 = 0.85$

$\log 8 = 0.9$

$\log 9 = 0.96$

$\log 10 = 1$

$\log 11 = 1.04$

$\log 1.8 = 0.26$.

eg:- $\log 50$

$= \log(5\times 10) = \log 5 + \overset{1}{\cancel{\log 10}} = 0.7 + 1 = 1.7$

eg:- $\log\sqrt{1000}$

$= \log 1000^{1/2} = \frac{1}{2}\log 1000 = \frac{1}{2}\log 10^{3} = \frac{3}{2}\log 10 = 1.5$

eg:- $\log 17$

$\log 17 = \dfrac{\log 18 + \log 16}{2}$ (average)

$\log 16 = \log 4^{2} = 2\log 4 = 2\times 0.6 = 1.2$.

$\log 18 = \log 9\times 2 = \log 9 + \log 2 = 0.96 + 0.3 = 1.26$

$\log 17 = \dfrac{1.2 + 1.26}{2} = 1.23$

eg:- $-\log 10^{-6} = 6\log 10 = 6$

eg:- $-\log 3\times10^{-6}$.

$$\boxed{-\log a\times10^{-b} = b-\log a}$$

$= 6-\log 3$

$= 6-0.48 = 5.52$

eg:- $-\log 2.1\times10^{-5}$

$=5-\log 2.1$

$=5-\log 2.1$

$=5-0.32$

⑦ Anti log :-

$$\boxed{\text{Antilog}(x) = 10^{x}}$$

$10^{0} = 1$

$10^{0.3} = 2$

$10^{0.48} = 3$

$10^{0.6} = 4$

$10^{0.7} = 5$

$10^{0.78} = 6$

$10^{0.85} = 7$

$10^{0.9} = 8$

$10^{0.96} = 9$.

$10^{1} = 10$

eg $\log 2 = 0.3$

Take antilog both sides

Antilog log 2 = Antilog 0.3

$2 = 10^{0.3}$.

eg:- $10^{-5.4}$ ← take just larger value

↳ convert into scientific notation

$= 10^{-6+0.6}$ $\{10^{a}\times10^{b} = 10^{a+b}\}$

$= 10^{-6}\times10^{0.6}$.

$= 4\times10^{-6}$.

Scientific Notation

$x\times10^{-y}$

$x\times10^{y}$

$x \to 1-10$

$y \to$ integer

eg $10^{-9.52} = 10^{-10+0.48}$

$= 10^{-10}\times10^{0.48} = 3\times10^{-10}$.

eg $10^{0.5}$
$= 10^{1-0.5}$
$= 10^{1} * 10^{0.5}$
$= 3.2 \times 10^{1-1}$
$= 3.2 \times 10^{0}$

Q Find the value of following:-

(i) $\log 30 = \log 3\times10 = \log 3 + \log 10 = 0.48 + 1 = 1.48$

(ii) $\log\sqrt{90} = \frac{1}{2}\log 9\times10 = \frac{1}{2}(\log 9 + \log 10) = \frac{1}{2}(0.96+1) = \cancel{\frac{1.96}{2}}\,0.98$

(iii) $\log 1000 = \log 10^{3} = 3\log 10 = 3$

(iv) $\log 19 = \frac{\log 18 + \log 20}{2} = \frac{\log 2 + \log 9 + \log 2 + \log 10}{2} = \frac{0.3+0.96+0.3+1}{2}\ \frac{2.56}{2}$
$= 1.28$

(v) $-\log 10^{-5} = 5\log 10 = 5$

(vi) $-\log 2\times10^{-5} = 5 - \log 2 = 5 - 0.3 = 4.7$

(vii) $-\log 5.5\times10^{-8} = 8 - \log 5.5 = 8 - 0.75 \quad 7.25$

viii) $-\log 2.2\times10^{-9} = 9 - \log 2.2 = 9 - 0.34 = 8.6$

ix) $10^{-3.3} = \cancel{\log}^{-4}\ 10^{-4+0.7} = 10^{0.7}\times10^{-4} = 5\times10^{-4}$

x) $10^{-6.52} = \cancel{\log}\,10^{-7+0.48} = \cancel{\log}\ 10^{-7}\times10^{+4.8} = 3\times10^{-7}$

xi) $10^{-3.31} = \log^{-4+0.7} \quad 5\times10^{-4}$.

xii) $\log 2\times10^{-5} = \cancel{-5}\ \log 2 + \log 10^{-5} \quad -5 + \log 2$
$= -5 + 0.3 = -4.7$

⇒ pH scale :-

* pH of solution can be calculated by

$$\boxed{pH = -\log[H^+]}$$

$[H^+]$ = concentration of H^+ ions in solution

* Similarly pOH of sol^n can be calculated by

$$\boxed{pOH = -\log[OH^-]}$$

$[OH^-]$ = concentration of OH^- ion in solution.

* If pH of solution is known then

$$\boxed{[H^+] = 10^{-pH}}$$

* If pOH of sol^n is known then

$$\boxed{[OH^-] = 10^{-pH}}$$

⇒ For any sol^n :-

$$\left.\begin{array}{l} \boxed{[H^+] \times [OH^-] = 10^{-14}} \\ \\ \boxed{pH + pOH = 14} \end{array}\right\} \text{At } 25^\circ C$$

* Acidic nature of solution is directly propotion $[H^+]$

$$\text{Acidic Nature} \propto [H^+] \propto \frac{1}{pH}$$

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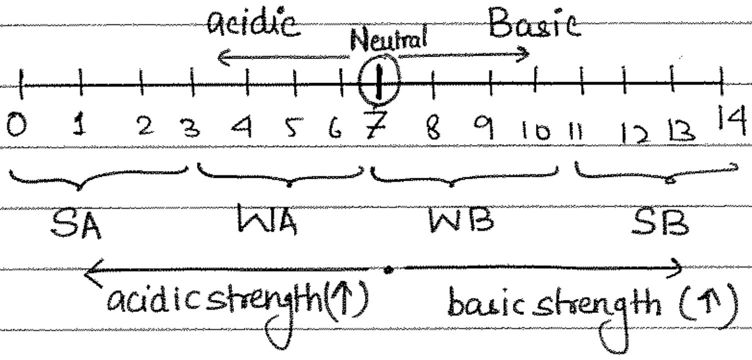
Basic nature $\propto [OH^-] \propto \frac{1}{[H^+]} \propto pH$

pH scale :- (At = 25°C)



⇒ **Neutral** $pH = pOH = 7$ $[H^+] = [OH^-] = 10^{-7}$

⇒ **Acidic** $pH < 7$ or $pOH > 7$ $[H^+] > [OH^-]$; $[H^+] > 10^{-7}$

⇒ **Basic** $pH > 7$ or $pOH < 7$ $[H^+] < [OH^-]$; $[H^+] < 10^{-7}$

Q Find the value of pH in each case :-

1. $[H^+] = 10^{-5} M$
2. $[H^+] = 2 \times 10^{-8} M$
3. $[H^+] = 3.5 \times 10^{-8} M$
4. pOH of solⁿ = 4.52
5. $[OH^-] = 5 \times 10^{-3} M$
6. 2×10^{-5} moles of H^+ ion present in 100 ml solⁿ.
7. 3×10^{20} OH^- ions are present in 500 ml solⁿ.

Solⁿ $pH = -\log[H^+]$

(i) $pH = -\log(10^{-5}) = 5$

(ii) $pH = -\log(2 \times 10^{-8}) = 8 - \log 2 = 8 - 0.3 = 7.7$

(iii) $pH = -\log(3.5 \times 10^{-6}) = 6 - \log 3.5 = 6 - 0.55 = 5.45$

iv) $pOH = 4.5$ $\quad pH + pOH = 14$

$pH = 14 - 4.5$

$= 9.5$

v) $[OH^-] = 5 \times 10^{-3} M$

$pOH = -\log(5 \times 10^{-3})$

$= 3 - \log 5 = 3 - 0.7$

$= 2.3$.

$pH + pOH = 14$

$pH = 14 - 2.3$

$= 11.7$

vi) $[H^+] = \frac{2 \times 10^{-5}}{4\cancel{00}} \times 1\cancel{000} = 2 \times 10^{-4}$

$pH = -\log 2 \times 10^{-4} = 4 - \log 2$

$= 4 - 0.3 = 3.7$

vii) $[OH^-] \frac{3 \times 10^{20}}{\cancel{500}} \times \overset{2}{\cancel{1000}} = 6 \times 10^{20}$

$pOH = -\log\left(\frac{6 \times 10^{20}}{6 \times 10^{23}}\right) = -(\cancel{\log 6} + \log_{10} \cancel{20}) = -\log 10^{-3}$

$= \cancel{-20} - \cancel{\log 6} \qquad = 3$

$= \cancel{-20} -$

$pH + pOH = 14$

$pH = 11$

Q. Calculate the concⁿ of $[H^+]$ ions in each case :-

(i) $[OH^-] = 5 \times 10^{-8}$

(ii) $pH = 5$

(iii) pH of soft drink is 4.7.

(iv) pOH of solⁿ is 9.48

Sol^n

(I) $[H^+][OH^-] = 10^{-14}$

$[H^+] = \frac{10^{-14}}{5\times10^{-8}} = 0.2 \times 10^{-14+8}$

$= 0.2\times10^{6}$.

(II) pH = 5 $\quad [H^+] = 10^{-5}$

(III) pH of soft drink = 4.7

$[H^+] = 10^{-4.7}$

$= 10^{-5+0.3} \quad .10^{0.3}\times10^{-5}$

$= 2\times10^{-5}$

(IV) pOH of sol^n 9.48

$[OH^-] = 10^{-9.48} = 10^{-10+0.52}$

$= 10^{0.52}\times10^{-10}$

$= 3.3\times10^{-10}$

$[H^+] = \frac{10^{-14}}{3.3\times10^{-10}} = 0.33\times10^{-4}$

Q. Calculate the number of H^+ ions present in a 100 ml solution of pH=5

$[H^+] = 10^{-5}$

$\frac{n}{V} = 10^{-5}$

$n = 10^{-5}\times\frac{1\cancel{00}}{10\cancel{00}} = 10^{-6}$.

no of ions $= 6\times10^{23}\times10^{-6}$

$= 6\times10^{17}$

Arrhenious theory :-

1. When an electrolyte is added in water, it gets split into two Oppositely charged ions that is Cation & Anion.

2. Overall solution is neutral i.e total positive charge is equal to total negative charge.

3. Number of +ve ions may or may not be equal to number of −ve ions.

4. Property of solution is due to its ions

5. An equilibrium is established b/w ionised & unionised part known as Ionic Equilibrium.

$$\underset{\text{unionised part}}{\underleftrightarrow{AB_{(aq)}}} \rightleftharpoons \underset{\text{ionsied part}}{\underleftrightarrow{A^+_{(aq)} + B^-_{(aq)}}}$$

$$\textcircled{K} = \frac{[A^+][B^-]}{[AB]}$$

ionisation Const or Dissociation const.

eg :- $A_3B_2 \rightleftharpoons 3A^{2+} + 2B^{3-}$

total +ve charge = +6

total −ve charge = −6.

Total charge = 0.

no of +ve ions = 3

no of −ve ions = 2.

Total no of ions = 5

⇒ Ostwald dilution Law :-

* Only applicable on weak electrolyte

A/c to this law when an aqueous solution of weak electrolyte is diluted then degree of ionisation of weak electrolyte increases

$$\boxed{\text{On dilution} \Rightarrow \alpha \uparrow} \quad \boxed{\alpha\uparrow \propto \sqrt{V\uparrow}}$$

* At infinite dilution $\alpha \sim 1$ or 100% dissociated i.e weak electrolyte behaves as strong electrolyte.

⇒ Factors affecting degree of Ionisation :-

1. TEMPERATURE :- On increasing the temp. degree of ionisation increases hence ionisation is a Endothermic process

$$AB \longrightarrow A^+ + B^- \qquad \Delta H = +ve$$

2. DILUTION :- On dilution, degree of ionisation increases

3. Nature of electrolyte (solute) :- Strong electrolyte ($\alpha = 1$)
Weak electrolyte ($\alpha < 1$)

4. Nature of solvent :- As dielectric const of solvent increases degree of ionisation also increases.

$$F = \frac{kq_1q_2}{r^2} = \frac{1}{4\pi\epsilon_0\epsilon_r}\frac{q_1q_2}{r^2} \qquad \downarrow F \propto \frac{1}{\epsilon_r\uparrow}$$

so less force of attraction
So easily breaks

H_2O (DC = 81)

D_2O (DC = 79)

Benzene (C_6H_6) (DC = 2.5)

CCl_4 (DC = 0)

(5) Mixing of Ions :—

(i) Common Ion effect :- When a strong electrolyte is added in an aqueous solution of weak electrolyte having common ions b/w them. Then degree of ionisation of weak electrolyte decreases this compound is called common Ion effect.

Backward ←

$\alpha \downarrow$

eg :— $\underset{\text{(Weak Electrolyte)}}{CH_3COOH} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$

$\underset{\text{(Strong electrolyte)}}{CH_3COONa} \rightleftharpoons CH_3COO^-_{(aq)} + Na^+_{(aq)}$

↳ common ion

$[H^+]\downarrow = pH\uparrow$

↳ acidic strength (↓)

Backward ←

$\alpha \downarrow$

eg :— $\underset{\text{(Weak acid)}}{H_2S} \rightleftharpoons 2H^+ + S^{2-}$ $[S^{2-}]\downarrow$

$HCl \longrightarrow H^+ + Cl^-$

↳ common ion

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(ii) Odd ion effect :- When a strong electrolyte is added in an aqueous solution of weak electrolyte having odd ions b/w them then degree of ionisation of weak electrolyte increases.

FORWARD $\alpha \uparrow$ ⟶

eg :- $CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)} \downarrow$ ← odd ion

$NaOH_{(aq)} \longrightarrow Na^+_{(q)} + OH^-_{(aq)}$

$\longrightarrow H_2O$ (weak electrolyte so doesn't dissociate)

Q In which of the following pair Common Ion effect is applicable

(1) $\overset{SA}{HCl} + \overset{SS}{NaCl}$

(II) $\overset{SB}{NaOH} + \overset{SA}{HCl}$

H(✓) ✓ (III) $CH_3COOH + HCl$

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

$HCl \longrightarrow H^+ + Cl^-$

(IV) $\overset{S.B}{Ba(OH)_2} + \overset{S.S}{BaCl_2}$

✓ (V) $NH_4OH + NH_4Cl$

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ ← CIE

$NH_4Cl \longrightarrow NH_4^+ + Cl^-$

⟵ Backward $[OH^-]\downarrow$ pH ↓

(VI) $\underset{SA}{HNO_3} + \underset{SS}{NaNO_3}$

Q When NH_4Cl is added in an aqueous solⁿ of NH_4OH. Then

(1) pH ↓

(2) $[OH^-] \downarrow$

(3) Basic strength ↓

✓ (4) All

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⇒ Water :-

1. Water is neutral

$$\left.\begin{array}{l} pH = pOH = 7 \\ [H^+] = [OH^-] = 10^{-7} \end{array}\right\} \text{at } 25°c$$

2. ρ of water = $1 gm/mL$ or $1 g/cc$

3. no of moles of H_2O in 1L water = 55.5 moles

$1L \rightarrow 1000ml \rightarrow 1000g \quad n = \frac{1000}{18}$

4. no of molecules of H_2O in 1L water = 55.5 Na

5. Concn of water = 55.5M.

6. Conc of H^+ and OH^- ion in water.

$[H^+] = 10^{-7}$ M

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

7. No of moles of H^+ and OH^- ion in 1L water.

$n_{H^+} = 10^{-7}$ moles

$n_{OH^-} = 10^{-7}$ moles.

8. No of H^+ and OH^- ions in 1L water

$N_{H^+} = 10^{-7} Na = 6.02 \times 10^{+23-7} = 6.02 \times 10^{16}$

$N_{OH^-} = 10^{-7} Na = 6.02 \times 10^{16}$.

9) Degree of Ionisation : (α)

$$H_2O \rightleftharpoons H^+ + OH^-$$

$t=0$ $\quad C \quad 0 \quad 0$

eq $\quad C - C\alpha \quad C\alpha \quad C\alpha$

$[H^+] = C\alpha$ $\qquad (C = 55.M)$

$10^{-7} = C\alpha$

$\frac{10^{-7}}{C} = \alpha = \frac{10^{-7}}{55.5} = 1.8 \times 10^{-9}$ or $1.8 \times 10^{-7}\,\%$.

Hence water is very weak electrolyte.

$C - C\alpha = [H_2O]$

$\underbrace{C(1-\alpha)}_{1} = [H_2O$

$C = H_2O$ (Hence conc of water doesn't changes.

10) Dissociation const of water :-

$$H_2O \rightleftharpoons H^+ + OH^-$$

$K_d = \frac{[H^+][OH^-]}{[H_2O]}$ $\qquad [H_2O] = 55.5 = \text{const}$

$Kd = \frac{10^{-7} \times 10^{-7}}{55.5} \Rightarrow \boxed{1.8 \times 10^{-16} = kd}$

⑪ Ionic product of water (kw) :-

$H_2O \rightleftharpoons H^+ + OH^-$

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

Since $[H_2O]$ = const & kd is const, so on multiplication we get,

$kd \times [H_2O] = [H^+][OH^-]$ $\boxed{kw = kd \times [H_2O]}$

$$\boxed{kw = [H^+][OH^-]}$$

At 25°C

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

$\therefore kw = 10^{-7} \times 10^{-7} = 10^{-14}$

$\boxed{kw = 10^{-14}}$

⑫ For any solution $[H^+] \times [OH^-] = 10^{-14} = kw$ } At 25°C

↳ At any temp $[H^+][OH^-] = kw$

$[H^+][OH^-] = kw$

Taking log both sides

$-\log[H^+][OH^-] = -\log kw$

$-(\log[H]^+ + \log[OH^-]) = -\log kw$

$= -\log[H^+] - \log[OH^-] = -\log kw$ $\boxed{-\log kw = pkw}$

$= \boxed{pH + pOH = pkw}$

At 25°C

$kw = 10^{-14}$, $pkw = 14$

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

$\boxed{pH + pOH = 14}$

3) For a neutral solution or water

* $[H^+] = [OH^-]$

$[H^+]^2 = kw$

$\boxed{[H] = [OH^-] = \sqrt{kw}}$

* $pH + pOH = pkw$

$pH = pOH$ (For neutral solⁿ)

$2pH = pkw$

$\boxed{pH = pOH = \frac{pkw}{2}}$

At 25°c

$kw = 10^{-14}$, $pkw = 14$

$[H^+] = [OH^-] = \sqrt{10^{-14}} = 10^{-7}$

$pH = pOH = 14/2 = 7$

⑭ Effect of temperature :-

$H_2O \rightleftharpoons H^+ + OH^-$; $\Delta H = +ve$ ENDO

$T\uparrow \Rightarrow \text{ENDO} \Rightarrow \text{Forward} \Rightarrow \alpha\uparrow \Rightarrow [H^+]\uparrow [OH^-]\uparrow \Rightarrow [H^+]\times[OH^-]\uparrow = k_w\uparrow$

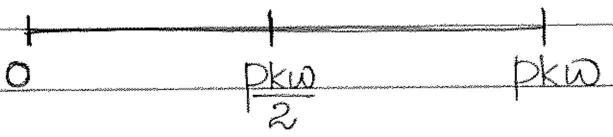
$T\uparrow \Rightarrow \alpha\uparrow \Rightarrow [H]\uparrow\ [OH]\uparrow \Rightarrow pH\downarrow\ pOH\downarrow \Rightarrow (pH+pOH)\downarrow \Rightarrow pk_w\downarrow$

Note :- On changing the temperature, water remain neutral

Temperature	25°C	90°C
① k_w	10^{-14}	10^{-12}
② pk_w	14	12
③ $[H^+]\times[OH^-]$	10^{-14}	10^{-12}
④ $pH + pOH = pk_w$	14	12
	For neutral solⁿ	
⑤ $[H^+] = [OH^-] = \sqrt{k_w}$	$= 10^{-7}$	10^{-6}
⑥ $pH = pOH = \frac{pk_w}{2}$	$= 7$	6
⑦ $[H^+] + [OH^-]$	$= 2\times10^{-7}$	2×10^{-6}

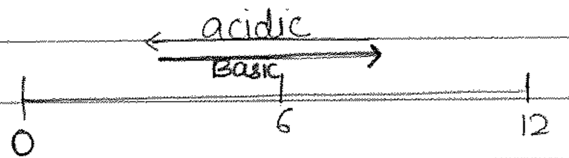
* If T↑ pH↓ . (Refrence temp = 25°C)

* pH scale at any temprature :-



eg At 90°C

$kw = 10^{-12}$ $pkw = 12$



$pH = 6.5$ (At = 25°C) = Acidic

$pH = 6.5$ (At = 90°C) = Basic

* $[H^+] = [H_3O^+]$

$$\boxed{kw = [H_3O]^+ \times [OH^-]}$$

⇒ Self Ionisation const or Auto ionisation const

eg $$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

accepts H+ forms

$$\boxed{K = [H_3O^+] \times [OH^-]}$$ $\therefore [H_3O^+] = [OH^-]$

Self ionisation const

eg $$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

one NH3 accept H+

one NH3 looses H+

$$\boxed{K = [NH_4^+][NH_2^-]}$$ $\therefore [NH_4^+] = [NH_2^-]$

Self ionisation const.

eg $HCOOH + HCOOH \rightleftharpoons HCOOH_2^+ + HCOO^-$

$$\boxed{k = [HCOO^-][HCOOH_2^+]} \qquad [HCOO^-] = [HCOOH_2^+]$$

self ionisation const

Q The pH of water is :-

[✓ (I) 7]

(II) <7

(III) >7

(iv) 6

Q The pH of water at 200k is :-

$T = 25°C = 298k$

$T\downarrow \Rightarrow [H^+]\downarrow \Rightarrow pH\uparrow$

(I) 7

[✓ (II) >7]

(III) <7

(iv) can't predict

Q At 100°c neutral solⁿ has $[H_3O] = 10^{-5.5}$ Then calculate the ionic product of water

$$[H_3O^+] = [OH^-] = 10^{-5.5}$$

$$kw = 10^{-5.5\times2} \Rightarrow \boxed{10^{-11} = kw}$$

$$pkw = -\log kw$$
$$= -\log 10^{-11}$$
$$= 11$$

Q Self ionisation const of pure acetic acid is 1.44×10^{-12} at 90°C. Then calculate the conc of acetate ion

$$2CH_3COOH \rightleftharpoons CH_3COO^- + CH_3COOH_2^+$$

$$Kw = [CH_3COO^-][CH_3COOH_2^+]$$

$$kw = [CH_3COO^-]^2$$

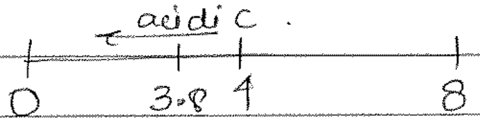
$$\sqrt{kw} = [CH_3COO^-]$$

$$\sqrt{\frac{144}{100}\times10^{-12}} = [CH_3COO^-]$$

$$= 12\times10^{-7} = [CH_3COO^-]$$

Q The pH of solⁿ is 3.8 at 100°C. What would be the nature of solⁿ of solⁿ and pOH of solⁿ at 100°C if kw at 100°C is 10-8.

$$pkw = -\log 10^{-8}$$
$$= 8$$



pH (3.8) = Acidic

pOH = 8 - 3.8
= 4.2

* kw doesn't depend on $[H^+]$ and $[OH^-]$ but depend upon Temperature.

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⇒ pH calculation :-

① pH of weak acidic :-

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

$\therefore [H^+] = [A^-]$

cation = anion

$t=0 \quad C \quad\quad 0 \quad 0$

normality

$t=t_{eq} \quad C-C\alpha \quad\quad C\alpha \quad C\alpha$

$$ka = \frac{\cancel{C}\alpha \times C\alpha}{\cancel{C}(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$\alpha << 1$. (α should be less than 5 %)

$1-\alpha \simeq 1$

$$\boxed{ka = C\alpha^2}$$

$$\alpha^2 = \frac{ka}{c}$$

$$\boxed{\alpha = \sqrt{\frac{ka}{c}}}$$ (Degree of ionisiation of weak acid)

$$[H^+] = C\alpha$$

$$= c\sqrt{\frac{ka}{c}} = \sqrt{\frac{C^2 \times ka}{c}} = \sqrt{kac}$$

$$\boxed{[H^+] = \sqrt{ka \times c}}$$

④ $\boxed{pH = \frac{1}{2}(pka - \log c)}$

Where pka = $-\log ka$

eg $ka = 1.8 \times 10^{-5}$

$pka = -\log 1.8 \times 10^{-5}$

$= 5 - \log 1.8$

$= 5 - 0.26$

$= 4.74$

I) PH calculation of weak base :-

Consider a monoacidic base.

$$BOH_{(aq)} \rightleftharpoons B^{+}_{(aq)} + OH^{-}_{(aq)}$$

C	0	0
$C - C\alpha$	$C\alpha$	$C\alpha$

C = initial con^n of weak base in normality
α = degree of ionisation of weak Base

① ionisation const of weak Base (kb)

$$\boxed{K_b = C\alpha^2}$$

② Degree of ionisation of weak base (α)

$$\alpha = \sqrt{kb/c}$$

③ Concⁿ of OH^- ion :-

$[OH^-] = C\alpha$

$[OH^-] = \sqrt{K_b \times C}$

Q. Calculate the pH of 0.1 M $CH_3COOH(aq)$ solⁿ whose degree of ionisation is 4% also calculate the concⁿ of H^+ ion and Hydroxyl ion $[OH^-]$ in solⁿ.

Solⁿ weak acid solution

$N = 0.1$

$[H^+] = C\alpha$

$= \frac{0.1}{10} \times \frac{0.04}{100} = 4 \times 10^{-3}$

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

$[OH^-] = \frac{10^{-14}}{4 \times 10^{-3}} = 0.25 \times 10^{-14+3}$

$= 0.25 \times 10^{-11}$

$pH = \frac{1}{2} pK_a - \log C$

$= \frac{1}{2}(4.4) - \log 0.1$

$= 2.2 - \log 0.1$

$= \cancel{2.1}$

$= 2.2 - \log 10^{-1}$

$= \cancel{2.2 + 1}$

$= \frac{2.6}{2} - \log 0.1$

$= 1.3 + 1 = 2.3$

$K_a = C\alpha^2$

$= 0.1 \times \left(\frac{4}{100}\right)^2$

$= 0.1 \times 4 \times 10^{-4}$

$= 4 \times 10^{-5}$

$pK_a = 5 - \log 4$

$= 5 - 0.6$

$= 4.4$

$= 0.1 \times 16 \times 10^{-4}$

$= 16 \times 10^{-5}$

$= 5 - \log 16$

$= 5 - 4 \times \log 4$

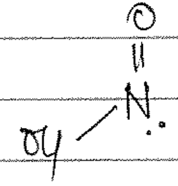
$\begin{array}{r} 0.6 \\ \times 4 \\ \hline 2.4 \end{array}$

$= 2.6$

$; 5 - 2.4$

Q Calculate pH of 2.5×10^{-1} M Nitrous acid (HNO_2) ~~ati~~ solⁿ if ionisation const of nitrous acid is 4×10^{-8}.

Solⁿ



$n = 1$ (valency)

$N = 2.5 \times 10^{-1}$

$ka = 4 \times 10^{-8}$

$\sqrt{kaC} = [H^+]$

$[H^+] = \sqrt{4 \times 10^{-8} \times 2.5 \times 10^{-1}}$

$= \sqrt{10 \times 10^{-8} \times 10^{-1}} = 10^{-4}$

$pH = -\log 10^{-4}$

$pH = 4$

Q Calculate the ionisation const of HCN if pOH of 2.5×10^{-1} M HCN solⁿ is 11 (weak acid)

~~$pOH = 2.5 \times 10^{-1}$ M~~

~~$-\log[OH] = 2.5 \times 10^{-1}$~~

~~$[OH^-] =$~~

$pOH = 11$

$[OH^-]$

$pH = 3$

$[H^+] = 10^{-3}$

$N = 2.5 \times 10^{-1}$ M

$[H^+] = \sqrt{ka \times c}$

$$\frac{(10^{-3})^2}{2.5 \times 10^{-1}} = ka = \frac{10^{-6} \times 10^{+1} \times \cancel{10}}{\cancel{25}}\, 0.4$$

$ka = 0.4 \times 10^{-5}$

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Q. If 2×10^{-3} mol of weak acid is present in 1L solution then calculate the percentage dissociation of weak given ionisation const of weak acid is 2×10^{-6}.

Sol

Solⁿ Consider monobasic.

$[C] = 2 \times 10^{-3} M$. $N = 2 \times 10^{-3} M$.

$Ka = C\alpha^2$

$\sqrt{\frac{ka}{c}} = \alpha$ $\alpha = \sqrt{\frac{\cancel{2} \times 10^{-6}}{\cancel{2} \times 10^{-3}}}$

$\alpha = \sqrt{10^{-6+3}} = \sqrt{10^{-3}}$

$= \sqrt{10 \times 10^{-4}}$

$= 10^{-2}\sqrt{10}$

$= 3.1 \times 10^{-2}$

% dissociation $= 3.1 \times (10^{-2}) \times 100$

$= 3.1\%$

Q. For a weak acid $\alpha = \frac{1}{1000\,c}$ calculate the pH.

$ka = \frac{1}{1000}$

$[H^+] = C\alpha$

$= \frac{1}{1000\cancel{c}} \times \cancel{c} = 10^{-3}$

$pH = -\log[H^+] = -\log 10^{-3}$

$= 3$

? The degree of ionisation of H_2S is 3% then calculate the following in 0.01 M H_2S solution.

① pH
② concⁿ of S^{2-}

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

Solⁿ $\alpha = 3\% = 3\times10^{-2}$

$C = 0.01M$ $N = 0.01\times2$
$= 0.02$

$H^+ = C\alpha$
$= 0.02\times3\times10^{-2}$
$= 6\times10^{-4}$
$pH = -\log 6\times10^{-4}$
$= 4 - \log 6$
$= 4 - 0.78$
$= 3.22$

$[H^+] = [S^{2-}]$
$[S^{2-}] = 6\times10^{-4}$

Q7 Calculate the pH of 0.1M $NH_3(aq)$ solⁿ if degree of ionisation of NH_3 is 10%

$\alpha = 10\%$. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$C = 0.1$ $N = 0.1$.

$[OH^-] = C\alpha$ $pOH = 2$
$=$ ~~0.1×0.01~~ 0.1×0.1 $pH = 14-2$
$=$ ~~10^{-3}~~ $= 10^{-2}$ $= 12$

Ⅲ pH of Strong Acid :-

concentration of H^+ ions in solution is equal to conc^n of strong acid in normality.

$[H^+] = [SA]$ = concentration of strong acid in normality.

$$\boxed{pH = -\log[H^+]}$$

Ⅳ pH of strong base :-

Concentration of OH^- ion in solution is equal to conc of strong base in normality.

$[OH^-] = [SB]$ = conc^n of strong base in normality

$$\boxed{pOH = -\log[OH^-]} \qquad pH = 14 - pOH$$

(* centimolar $= 10^{-2}M$)

Q. Calculate the pH in each case ?

(1) $\frac{M}{100}$ HCl sol^n $\Rightarrow$ $10^{-2}M$ HCl $N = 10^{-2}N$. $[H^+] = 10^{-2}$ $pH = 2$.

(2) $\frac{N}{100}$ H_2SO_4 sol^n $\Rightarrow$ $10^{-2}N$ HCl $[H^+] = 10^{-2}$ = $pH = 2$

(3) centimolar H_2SO_4 sol^n $10^{-2}M$ $[H^+] = 2\times10^{-2}$ $pH = 2 - \log 2$
$= 2 - 0.3 = 1.7$

(4) $10^{-2}M$ $Ba(OH)_2$ sol^n $C = 10^{-2}$ $N = 10^{-2}\times 2$ $[OH^-] = 2\times10^{-2}$ $pOH = 2 - \log 2$
$= 2 - 0.3$
$= 1.7$
$pH = 14 - 1.7$
$= 12.3$

(5) 49 g of H_2SO_4 present in 10 L sol^n

$$C = \frac{49}{98\times10} = \frac{1}{20} \quad N = \frac{1}{20}\times2 = 10^{-1} \quad [H^+] = 10^{-1}$$

$pH = 1$

Q H_2X is a diabasic acid which dissociates completely. Calculate the conc^n of H_2X if the pH of sol^n is 2. In molarity & normality

$pH = 2$

$[H^+] = 10^{-2}$

$[H^+] = \cancel{0.3N}$. $[H_2X] = 10^{-2} N$

Molarity $= \frac{\cancel{0.3}}{\cancel{2}} = \cancel{0.15}$ $\frac{10^{-2}}{2} = 0.5 \times 10^{-2} M$

Q $M(OH)_2$ is a Strong electrolyte. Calute the pH of solution in which 2 milli mol of $M(OH)_2$ is present in 40 ml of sol^n

2 milli mol $= 2 \times 10^{-3}$ mol

$C\,[M(OH)_2] = \frac{2 \times 10^{-3}}{4\cancel{0}} \times 100\cancel{0}$

$= \frac{1}{2} \times 10^{-1}$

$[OH^-] = \frac{1}{2} \times 10^{-1} = 0.5 \times 10^{-1}$

$pOH = -\log OH^-$

$= -\log 0.5 \times 10^{-1}$

$= 1 - \log 0.5$

$= 1 -$

$[OH^-] = 0.5 \times 2 \times 10^{-1}$

$= 10^{-1} N$

$pOH = -\log OH^-$

$= 1$

$pH = 14 - 1$

$= 13$

Q Calculate the amount of KOH present in 500cc of KOH solution whose $pH = 12$

$[H^+] = 10^{-12}$

KOH

$$\begin{array}{r} 39 \\ 16 \\ 1 \\ \hline 56 \end{array}$$

~~KOH = 10^{-12} N = 10^{-12} M~~

~~moles of KOH = $10^{-12} \times \frac{500}{1000}$~~

~~= 5×10^{-13}~~.

$[OH^-] = 10^{-2}$

KOH = 10^{-2} N = 10^{-2} M

moles of KOH = $10^{-2} \times \frac{\cancel{500}}{\cancel{1000}}$ = 5×10^{-3}.

Gwt = $5 \times 10^{-3} \times (56)$

Q pH of 10^{-4} M $\underbrace{HCOOH}_{\text{weak acid}}$ solution is.

(I) 4

(II) <4

✓(III) >4

(IV) 2

Assuming strong acid

pH = 4

pH > 4 (As weak acid)

Q.

⇒ Law of Dilution :-

Equivalent or moles of solute before dilution equals to equivalent or moles of solute after dilution

N/n before dilution = N/n after dilution

N_i, N_f = conc of solution before and after dilution
v_i, v_f = volume of solution before and after birth

$\boxed{N_i v_i = N_f v_f}$ or $\boxed{M_i v_i = M_f v_f}$

Volume of water added = $v_f - v_i$.

Q 10^{-2} M HCl solution is diluted 100 times then pH of solution will.

(1) increase by 4 unit
(2) increase by 2 unit
(3) decreases by 4 unit
(4) decreases by 2 unit.

pH without dilution = 2

$V_i \rightarrow 1$
$V_f \rightarrow 100$

initial conc of HCl = 10^{-2} M moles = 10^{-2} mole

$$\text{conc of HCl}_{\text{final}} = \frac{10^{-2}}{100} = 10^{-4}$$

$$\begin{aligned} pH &= -\log H^+ \\ &= -\log 10^{-4} \\ &= 4 \end{aligned}$$

(increase by 2 unit)

Q The pH of 1 L HCl solution is 2 calculate the volume of water required to be added to change its pH to 5

$pH = 2$ $\quad$ $[H] = 10^{-2}$

$pH = 5$ $\quad$ $[H] = 10^{-5}$

$M_iV_i = M_fV_f$

$10^{-2} \times 1 = 10^{-5} \times V_f$

$V_f = \frac{10^{-2}}{10^{-5}} = 10^{3} L$

Volume of water added = 1000 − 1
= 999 L

Q The pH of 10L HCl solⁿ is 2. Calculate the number of moles of HCl removed so as to change the pH to 4

$pH = 2$ $\quad$ $V = 10 L$

$[H] = 10^{-2}$

$V = 10$ $\quad$ $pH = 4$

$[H] = 10^{-4}$

$\frac{n}{V} = 10^{-2}$

$n_1 = 10^{-2} \times 10$
$= 10^{-1}$

$n_2 = 10^{-4} \times 10$
$= 10^{-3}$

$\Delta n = n_1 - n_2 = 10^{-1} - 10^{-3}$

$= \frac{1}{10} - \frac{1}{1000}$ $\quad$ $= \frac{1\cancel{0}00-1\cancel{0}}{10\cancel{0}0}$

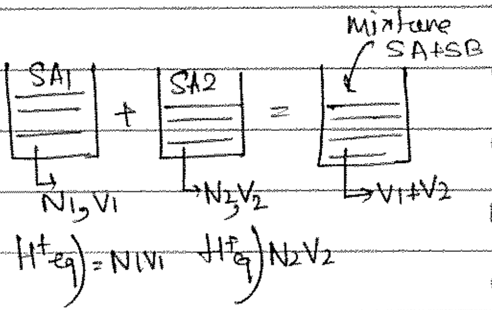
$= \frac{99\cancel{0}}{100\cancel{0}} = 0.\cancel{9}9$ mole

$= \frac{100-1}{1000} = \frac{99}{1000}$

$= 0.099$

⇒ pH of mixture of strong acid :-

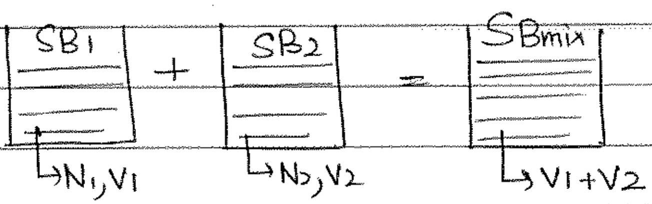
N_1, N_2 = conc of SA1 & SA2 solution in Normality
V_1, V_2 = volume of SA1 & SA2 solution.



After mixing

$$\boxed{[H^+] = \frac{N_1V_1 + N_2V_2}{V_1+V_2}}$$

⇒ pH of mixture of strong base :-



$$\boxed{[OH^-] = \frac{N_1V_1 + N_2V_2}{V_1+V_2}}$$ ← always in Normality.

Q Calculate the pH of mixture formed by mixing 100 mL, $\frac{M}{100}$ HNO_3 + 200 mL, $\frac{M}{200}$ H_2SO_4 + 800 mL, $\frac{M}{100}$ HCl

$$[H^+] = \frac{N_1V_1 + N_2V_2 + N_3V_3}{V_1+V_2+V_3}$$

$$= \frac{\frac{1}{\cancel{100}} \times \cancel{100} + \frac{1}{\cancel{200}} \times 2 \times \cancel{200} + \frac{1}{\cancel{100}} \times 8\cancel{00}}{1100}$$

$$= \frac{1+2+8}{1100} = \frac{\cancel{11}}{\cancel{11}00} = 10^{-2}$$

$$pH = -\log 10^{-2} = 2$$

Q Calculate pH of mixture formed by mixing 0.05 M, 100 ml $Ba(OH)_2$ solution + 0.1 M, 400 ml NaOH + 500 ml water

$$[OH^-] = \frac{N_1V_1 + N_2V_2}{V_1 + V_2 + V_{H_2O}}$$

$$= \frac{0.05 \times 2 \times 100 + 0.1 \times 400}{100 + 400 + 500}$$

$$= \frac{10 + 40}{1000} = \frac{5\cancel{0}}{100\cancel{0}} = 0.05$$

$$[H^+] = \frac{10^{-14} \times \overset{2}{\cancel{100}}}{0.\cancel{05}} = 2 \times 10^{-13}.$$

$$pH = 13 - \log 2$$
$$= 13 - 0.3 = 12.7$$

Q. Calculate the pH of solution formed by mixing a solution of pH = 2, 100 ml with pH = 3, 200 ml.

$pH = 2$	$pH = 3$
$[H^+] = 10^{-2}$	$[H] = 10^{-3}$
$V = 100ml$	$V = 200ml$
$eq = 10^{-2} \times 100$	$eq = 10^{-3} \times 200ml$

$$H^+ = \frac{10^{-2} \times 100 + 10^{-3} \times 200}{300}$$

$$= \frac{1 + 0.2}{300} = \frac{\overset{4}{\cancel{12}}}{\cancel{300} \times 10} = 4 \times 10^{-3}$$

$$pH = -\log 4 \times 10^{-3} = 3 - \log 4 = 3 - 0.6 = 2.4$$

2. Calculate the pH of solution formed by mixing equal volume of of solution having pH = 3 and pH = 3 & pH = 4

$[H^+]_1 = 10^{-3}$ $[H^+]_2 = 10^{-3}$ $[H^+]_3 = 10^{-\cancel{3}4}$.

eq $H^+ = 10^{-3} \times V$ eq $H^+ = 10^{-3} v$ eq $H^+ = 10^{-4} v$

$$[H^+] = \frac{(10^{-3} + 10^{-3} + 10^{-4})\cancel{v}}{3\cancel{v}}$$

$$= \frac{10^{-3}}{3}(1 + 1 + 0.1)$$

$$= \frac{\overset{7}{\cancel{21}} \times 10^{-3}}{\cancel{3} \times 10} = 7 \times 10^{-4}$$

$$pH = -\log 7 \times 10^{-4}$$

$$= 4 - \log 7$$

$$= 4 - 0.84 \quad = 3.15$$

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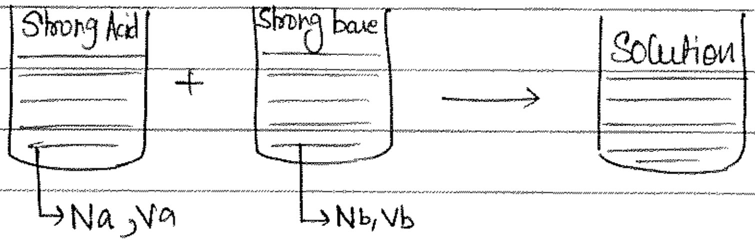
(VII) pH of mixture of strong Acid with strong base :- .



Case I : $N_aV_a = N_bV_b$.

Neutral .

$pH = 7$.

Case II : $N_aV_a > N_bV_b$

Acidic .

$pH < 7$.

$$\boxed{[H^+] = \frac{N_aV_a - N_bV_b}{V_a + V_b}}$$

Case III : $N_bV_b > N_aV_a$.

Basic .

$pH > 7$

$$\boxed{[OH^-] = \frac{N_bV_b - N_aV_a}{V_a + V_b}}.$$

N_a, N_b = concⁿ of strong acid and strong base in normality .
V_a, V_b = Volume of strong acid & strong base solution .

Q Calculate pH of solution formed by mixing 100ml, 0.2M NaOH with 900 ml, 0.1M H_2SO_4

Sol^n $Na = N_{H_2SO_4} = 0.1 \times 2$

$= 0.2$

$N_{H_2SO_4} V_{H_2SO_4} = \frac{0.2 \times \cancel{900}}{\cancel{1000}} = \frac{1.8}{10}.$

$N_{NaOH} V_{NaOH} = \frac{0.2 \times \cancel{100}}{\cancel{1000}} = \frac{0.2}{10}$

$$\begin{array}{r} 0.18 \\ \underline{0.02} \\ 0.16 \end{array}$$

$N_{solution} = \frac{\frac{1.8}{10} - \frac{0.2}{10}}{\frac{\cancel{1000}}{\cancel{1000}}} = 0.18 - 0.02$

$= 0.16$

$pH = -\log 16 \times 10^{-2}$

$$\begin{array}{r} 0.6 \\ \underline{\times 4} \\ 02.4 \end{array}$$

$= 2 - \log 16$

$$\begin{array}{c} 23 \\ 16 \\ | \\ 40 \end{array}$$

$= 2 - \cancel{2} \log 4$

$= 2 - \cancel{2} \times 0.6$

$= 2 - 1.2 = 0.8$

Q. Calculate the pH of sol^n formed by mixing 49gm H_2SO_4 with 80gm NaOH to form 100L sol^n

$n_{H_2SO_4} = \frac{49}{98} = \frac{1}{2}.$ $n_{NaOH} = \frac{\cancel{80}}{\cancel{40}} 2.$

$Feq_{H_2SO_4} = \frac{1}{2} \times 2 = 1.$ $Feq_{NaOH} = 2.$

Conc^n of solution $= \frac{2-1}{100} = \frac{1}{100}$ $pH = -\log 10^{-2}$

$p\overset{2}{OH} + pOH = 14$ $pH = 12$ $= 2$

VII pH of very dilute solⁿ of strong acid or strong base :-

If concⁿ of strong acid less than or equal to 10^{-7} then we have to consider the conc of H^+ from water also ($C = 10^{-7}_N, 10^{-8}N, 10^{-9}N, \ldots$)

$$[H^+] = [SA] + [H^+]_{H_2O}$$ ← In normality.

$$\boxed{[H^+] = [SA]_N + 10^{-7}}$$

Value of pH ranges from 6.7 to 7 .

For strong base :-

$C \leq 10^{-7}N$, we have to consider the conc of $OH^{\ominus}$ from water also. ($C = 10^{-7}N, 10^{-8}N, 10^{-9}N \ldots\ldots$)

$$[OH^-] = [SB]_N + [OH^-]_{H_2O}$$

$$\boxed{[OH^-] = [SB]_N + 10^{-7}}$$

Value of pH → 7 to 7.3 .

Q. The pH of $10^{-7}M$ HCl solⁿ is

$$[H^+] = 10^{-7} + 10^{-7} = 2 \times 10^{-7}$$

$$pH = -\log 2 \times 10^{-7} = 7 - \log 2$$
$$= 7 - 0.3$$
$$= 6.7$$

If conc^n of solution is C and if it is n times diluted then

$$\boxed{C \xrightarrow[\text{dilute}]{n\text{ times}} \frac{C}{n}}$$

Q 10^{-5} M HCl solution is 1000 times dilute calculate the pH

$$[C] = \frac{10^{-5}}{1000} = 10^{-8} \qquad \left(C \xrightarrow[\text{dilute}]{1000\text{ times}} \frac{C}{1000} \right)$$

$$[H^+] = 10^{-8} + 10^{-7}$$
$$= 10^{-7}\left(\frac{1}{10} + 1\right)$$
$$= 10^{-8}(11)$$
$$= 11 \times 10^{-8}$$
$$pH = -\log 11 \times 10^{-8}$$
$$= 8 - \log 11$$
$$= 8 - 1.04$$
$$= \underline{\underline{6.96}}$$

Q The pH of 10^{-11} M NaOH sol^n is .

~~(1) 11~~
(2) 3
(3) 7
(4) 7.003

IX pH of mixture of weak acid :-

$$[H^+] = C_1\alpha_1 + C_2\alpha_2$$

$$[H^+] = \sqrt{ka_1 c_1 + ka_2 c_2}$$

C_1, C_2 → conc of weak acid in normality

Q Calculate the pH of mixture of 0.2M CH_3COOH ($ka = 2\times10^{-5}$) with 0.4M C_6H_5-COOH ($ka = 3\times10^{-5}$)

WA + WA

$$[H^+] = \sqrt{2\times10^{-5}\times0.2 + 3\times10^{-5}\times0.4}$$

$$= \sqrt{0.4\times10^{-5} + 1.2\times10^{-5}}$$

$$= \cancel{10^{-5}}\sqrt{\cancel{1.6}} = \cancel{10^{-5}}\sqrt{\cancel{16/40}} = 4\times10^{-3}$$

$$pH = -\log 4\times10^{-3}$$

$$3 - \log 4$$

$$= 3 - 0.6 = 2.4$$

X pH of mixture of weak acid with strong acid.

$[H^+] = [SA]_N$ (Due to common Ion effect).

Backward $\alpha \downarrow$

eg

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

$$HCl \rightarrow Cl^- + H^+$$

$$\boxed{\alpha = \frac{(ka)_{WA}}{[SA]_N}}$$

$$\underset{C-C\alpha}{CH_3COOH} \rightleftharpoons \underset{C\alpha}{CH_3COO^-} + \underset{C\alpha}{H^+}$$

$$\underset{a}{HCl} \longrightarrow \underset{a}{H^+} + \underset{a}{Cl}$$

Q Calculate the degree of ionisation and conc of formate ion in 0.01M Formic acid solution in presence of 0.07 M HCl solⁿ. (Ka of HCOOH = 1.8×10^{-5})

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

$$\begin{matrix} c & 0 & 0 \\ c-c\alpha & c\alpha & c\alpha \end{matrix}$$

$$H \longrightarrow H^+ + Cl^-$$

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

$[H^+]_{net} = c\alpha + a$

$\simeq a$

$$Ka = \frac{c\alpha\, c\alpha}{c(1-\alpha)} = \frac{c^2\alpha^2}{c(1-\alpha)}$$

But when H+ is considered by SA

$$Ka = \frac{a \times \cancel{c}\alpha}{\cancel{c}(1-\alpha)} = \frac{a\alpha}{(1-\alpha)}$$

Since to common ion effect α of WA ↓ ∴ α very small

$(1-\alpha) = 1$

$Ka = a\alpha$

$$\alpha = \frac{ka}{a} = \frac{1.8 \times 10^{-5} \times 100}{0.01}$$

$\alpha = 1.8 \times 10^{-3}$

$[HCOO^-] = c\alpha$

$= 0.01 \times 1.8 \times 10^{-3}$

$= 1.8 \times 10^{-5}$

⇒ Hydrolysis of salt :-

$$\text{Acid} + \text{Base} \longrightarrow \text{Salt} + H_2O \quad , \quad \Delta H = -ve$$

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{NaOH} \Longrightarrow \underset{\underset{\text{frome Base}}{\uparrow}}{\overset{+}{Na}}\underset{\underset{\text{from acid}}{\nwarrow}}{\overset{-}{Cl}} + H_2O \qquad \Delta H = -ve$$

$$\underset{\underset{\text{frome Base}}{\downarrow}}{B^+}\,\underset{\underset{\text{from Acid}}{\searrow}}{A^-}$$

⇒ Types of salt :

① Normal Salt / General Salt / Simple Salt :- (No replacable H^+ and OH^- ions

eg. $NaCl$, Na_2SO_4, CH_3COONa, $HCOONa$, etc (formed by complete neutralisation of Acid & Base

$$\left.\begin{array}{l} \underset{\underset{1OH^-}{\downarrow}}{NaOH} + \underset{\underset{1H^+}{\downarrow}}{HCl} \longrightarrow NaCl \\[2em] \underset{\underset{1H^+}{\downarrow}}{HCOOH} + \underset{\underset{1OH^-}{\downarrow}}{NaOH} \longrightarrow HCOONa \end{array}\right\} \text{Normal Salt}$$

$$\underset{\underset{1OH^-}{\downarrow}}{NaOH} + \underset{\underset{2H^+}{\downarrow}}{H_2CO_3} \longrightarrow \underset{\underset{(\text{Acidic Salt})}{\downarrow}}{NaHCO_3}$$

② Acidic Salt :- (Incomplete neutralisation of Acid)

$NaHSO_4$, NaH_2PO_4, Na_2HPO_4, NaH_2PO_3, etc.

$$\underset{1OH^-}{\underset{\downarrow}{NaOH}} + \underset{2H^+}{\underset{\downarrow}{H_3PO_3}} \longrightarrow NaH_2PO_3 \quad \{\text{Acidic salt}\}$$

(Replacable ions)

$$\underset{2OH^-}{\underset{\downarrow}{2\,NaOH}} + \underset{2H^+}{\underset{\downarrow}{H_3PO_3}} \longrightarrow Na_2HPO_3 \quad \{\text{Neutral Salt}\}$$

(Replacable ions)

eg

$$\underset{1OH^-}{\underset{\downarrow}{NaOH}} + \underset{2H^+}{\underset{\downarrow}{H_2S}} \longrightarrow NaHS \quad (\text{Acidic})$$

$$\underset{1OH^-}{\underset{\downarrow}{NaOH}} + \underset{2H^+}{\underset{\downarrow}{H_2SO_4}} \longrightarrow NaHSO_4 \quad (\text{Acidic})$$

$$\underset{(\text{Normal})}{NaH_2PO_2} \longrightarrow \underset{1OH^-}{\underset{\downarrow}{NaOH}} + \underset{1H^+}{\underset{\downarrow}{H_3PO_2}}$$

③ Basic Salt :-

eg $Zn(OH)Cl$, $Mg(OH)Br$, $Fe(OH)Cl_2$, etc .

④ Double Salt :-

(Mohr's Salt)
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ vf = 4

(Pottash Allum)
$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ vf = 8

⑤ Mixed Salt :- (More than one type of cation or more than one type of anion)

eg $NaKSO_4$, $NaKRbPO_4$, $Ca(OCl)Cl$.

$$NaOH + H_2SO_4 \longrightarrow NaHSO_4$$

$$KOH + NaHSO_4 \longrightarrow NaKSO_4$$

$$\downarrow$$

$$Na^+ K^+ SO_4^{2-}$$

$$NaKRbPO_4 \qquad Ca(OCl)Cl$$

$$\downarrow \quad \downarrow \qquad \downarrow$$

$$Na^+ K^+ Rb^+ \; PO_4^{3-} \qquad Ca^{2+} OCl^- Cl^-$$

Q Identify the type of salt :-

(i) $NaNO_3$ ⟶ neutral
(ii) Na_3PO_4 ⟶ neutral .
(iii) $HCOONH_4$ ⟶ neutral
(iv) Na_2S ⟶ neutral
(v) $Mg(OH)Cl$ ⟶ Basic
(vi) $NaKCO_3$ ⟶ Mixed

→ Conjucate acid base pair :- (CABP)

* Two species having a difference of 1OH and 1H+ ion are known as conjucate acid base pair.

* The conjucate of strong is weak while the conjucate of weak is strong.

$Hcl \longrightarrow H^+ + cl^-$

Strong Acid — Weak conjucate base (non reactive) (non reactive)

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

Weak acid ka — Strong conjucate base kb

$NH_4OH \longrightarrow NH_4^+ + OH$

Weak Base — Strong conjucate Acid

$NaOH \longrightarrow Na^+ + OH^-$.

Strong base — Weak conjucate acid (non reactive) (non reactive)

→ Relation b/w ka and kb of CABP :-

$$\boxed{\begin{array}{c} ka \times kb = kw \\ pka + pkb = pkw. \end{array}}$$

At 25°C :-

$$\boxed{\begin{array}{c} ka \times kb = 10^{-14} \\ pka + pkb = 14 \end{array}}$$

eg NH_4OH / NH_4^+.

Base. / CA.

$\downarrow$ $kb = ?$ $\quad$ $\downarrow$ $ka = 10^{-6}$

$ka \times kb = 10^{-14}$.

$kb = 10^{-8}$.

Q Find pka of HCN (If the ionisation const kb of $CN^{\ominus}$ is 10^{-4} then calculate the value of pka of HCN)

kb of $CN^- = 10^{-4}$

$ka \times kb = 10^{-14}$

$ka = 10^{-10}$.

$pka = -\log 10^{-10}$

$= 10$

⇒ Salt Hydrolysis :-

* The process in which the cation or anion or both reacts with water so as to change the concentration of H^+ and OH^- ion is known as salt hydrolysis.

* Salt hydrolysis is the reverse of neutralisation reacⁿ.

(Neutralisation): $A + B \longrightarrow \text{salt} + H_2O$. ; $\Delta H = -ve$

(Salt hydrolysis): $\text{Salt} + \text{water} \longrightarrow A + B$; $\Delta H = +ve$.

TRICK :-

Cation from SB → SB SA ← Anion from SA

SB SA → Sepctator (No reacⁿ)

WA WB → Workes (React) (Hydrolysis)

WA SB: WA → Worker (React) (Hydrolysis); SB → Spectator.

* {The ion which comes from strong acid or strong base doesn't undergo hydrolysis while the ion which comes from weak acid or weak base undergoes Hydrolysis}

eg $NaNO_3$
SB SA
(no hydrolysis)

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I)
⇒ Hydrolysis of Strong Acid Strong Base type of salt (SASB) :-

eg NaCl , Na_2SO_4 , $NaClO_4$, K_2SO_4 , $NaNO_3$, etc

* No hydrolysis of this salt takes place .
* Solution is neutral .
* $pH = 7$
* No effect on litmus .

II) Hydrolysis of WBSA type salt :-

eg :- NH_4Cl , $(NH_4)_2SO_4$, $CaSO_4$, $CaCl_2$, NH_4NO_3 , NH_4Br , etc

* Cationic hydrolysis
* Acidic in nature .
* Blue litmus turns Red .
* $pH < 7$.

* Hydrolysis const (Kh) :-

$$\boxed{K_h = \frac{K_w}{K_b}}$$

* kw = Ionic product of water
* kb = Ionisation const of weak base .
from which this WBSA salt is formed .

* Degree of hydrolysis (h) :-

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

	c	0	0
t=teq	0	c	c

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

	c	0	0	0
t=teq	c-ch		ch	ch

$$kh = \frac{ch \times ch}{c(1-h)} = \frac{c^2h^2}{c(1-h)} = \frac{ch^2}{(1-h)}$$

$$h << 1 \quad . \quad h \simeq 1$$

✓ $\boxed{kh = ch^2}$

✓ $\boxed{h = \sqrt{\frac{kh}{c}}}$ C= initial conc of salt in Normality.

$\boxed{h = \sqrt{\frac{kw}{kb \times c}}}$. Note: $h \propto \frac{1}{\sqrt{c}}$ $c\downarrow h\uparrow$

* conc of H+ ion :-

$$[H^+] = ch$$

$$[H^+] = \sqrt{kh \times c}$$

$$[H^+] = \sqrt{\frac{kw \times c}{kb}}$$

* **pH of solution :-**

$$\boxed{pH = 7 - \frac{1}{2} pK_b - \frac{1}{2}\log c}$$

$$pH = -\log[H^+]$$
$$= -\log\left(\frac{K_w \times C}{K_b}\right)^{1/2}$$
$$pH = \frac{1}{2} pK_w - \frac{1}{2}\log pK_b - \frac{1}{2}\log c$$

Note :- On increasing the initial conc of salt pH of solution decreases.

II) Hydrolysis of WASB type of salt :-

eg* CH_3COONa, $NaCN$, KCN, K_2CO_3, Na_2CO_3, Na_2S, $HCOONa$, etc

- * Anionic hydrolysis
- * Basic
- * $pH > 7$
- * Red litmus turns into Blue.

$\underleftrightarrow{WA}\ \underleftrightarrow{SB}$

Anion cation.

worker

So hydrolysed

* Hydrolysis const (kh):

$$\boxed{k_h = \frac{k_w}{k_a}}$$

kw = ionic const of water

ka = ionisation const of weak acid from which this salt is formed.

* Degree of hydrolysis (h) :- (How much the ions are hydrolysed or reacted with water)

$$\begin{array}{ccccc} CH_3COONa & \rightleftharpoons & CH_3COO^- & + & Na^+ \\ c & & 0 & & 0 \\ 0 & & c & & c \end{array}$$

$$\begin{array}{ccccccc} CH_3COO^- & + & H_2O & \rightleftharpoons & CH_3COOH & + & OH^- \\ c & & 0 & & 0 & & 0 \\ c - c\alpha & & - & & ch & & ch \end{array}$$

$$\boxed{K_h = Ch^2}$$

$$\boxed{h = \sqrt{\frac{K_h}{C}}}$$

$$\boxed{h = \sqrt{\frac{K_w}{K_a \times C}}}$$

C = initial conc of salt in Normality

Note :- $h \propto \frac{1}{\sqrt{C}}$

* conc of $OH^{\ominus}$ ion

$$[OH^-] = Ch$$

$$[OH^-] = C\sqrt{\frac{K_h}{C}} = \sqrt{K_h \times C}$$

$$[OH^-] = \sqrt{\frac{K_w}{K_a} \times C}$$

pH of solution :-

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

$$\boxed{pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C}$$

$pK_a = -\log K_a$

Note :- On increasing the initial conc of salt pH of solution increases

(IV) Hydrolysis of WAWB type salt :-

eg :- NH_4CN, CH_3COONH_4, $HCOONH_4$, $(NH_4)_2CO_3$, etc.

* Maximum hydrolysis of this salt takes place.
* Almost neutral

* Hydrolysis const (Kh)

$$\boxed{kh = \frac{kw}{ka \times kb}}.$$

* **Degree of hydrolysis (h) :-**

$$CH_3COONH_4 \longrightarrow CH_3COO^- + NH_4^+$$

$t=0$ c 0 0
$t=t_{eq}$ 0 c c

$$CH_3COO^- + NH_4^- + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

c c 0 0
c-ch c-ch ch ch

$$kh = \frac{ch \times ch}{c(1-h) \times c(1-h)} = \frac{h^2}{1-h^2} \qquad 1-h^2 \simeq 1$$

$$kh = h^2$$

$$\boxed{h = \sqrt{kh}}$$

$$\boxed{h = \sqrt{\frac{kw}{ka \times kb}}}$$

Note :- 'h' doesn't depend on initial conc of WAWB salt.

$$\boxed{[H^+] = ka \times h}$$
$$\boxed{[OH^-] = kb \times H}$$

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

$$ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$\frac{ka\,[CH_3COOH]}{[CH_3COO^-]} = [H^+]$$

$$[H^+] = ka \times \frac{\cancel{c}h}{\cancel{c}(1-h)}$$
$$= ka \times h$$

pH of solution :-

$$\boxed{pH = 7 + \tfrac{1}{2}pka - \tfrac{1}{2}pkb}$$

pH of this sol^n do not depend on initial conc^n of salt.

* If

$ka = kb$	Neutral pH = 7	Neutral hydrolysis
$ka > kb$	Acidic pH < 7	Cationic Anionic hydrolysis
$kb > ka$	Basic pH > 7	Anion Cationic hydrolysis

1. Complete the table :-

Salt	Nature	pH	Hydrolysis
$FeCl_3$ WB SA	Acidic	⇒ less than 7	cationic hydrolysis
$NaNO_3$ SB SA	Neutral	= 7	X
$NaCN$ SB WA	Basic	⇒ greater than	Anionic hydrolysis

Q. Which of the following salt undergoes hydrolysis.

(i) $NaNO_3$) SASB

(ii) $NaClO_4$) SASB

(iii) Na_2SO_4) SASB

(iv) $CaSO_4$
WB SA.

Q. Which salt has maximum degree of hydrolysis.

(1) $CH_3COONa \longrightarrow$ WASB

(2) $NaCN \longrightarrow$ SBWA

(3) $AgCN \longrightarrow$ WAWB $\longrightarrow Ag^+ + CN^- \longrightarrow \overset{WB}{AgOH} + \overset{WA}{HCN}$
(Hydrolysis max^m)

(4) $(CH_3COO)_2Ba \longrightarrow$ WASB.

Q Which of the following has max^{m} degree of hydrolysis.

1. 0.1 M CH_3COONa
2. 0.01 M CH_3COONa
3. 0.001 M CH_3COONa.
4. All have same extent of hydrolysis.

Sol^n $h \propto \frac{1}{\sqrt{C}}$ $C\downarrow$ $h\uparrow$ So 0.001 M CH_3COONa (has max degree of hydrolysis).

Q Which of the following has max^{m} degree of hydrolysis.

(I) 0.01 M CH_3COONH_4
(II) 0.001 M CH_3COONH_4
(III) 0.1 M CH_3COONH_4
[✓ (IV)] all have same degree of hydrolysis

As $h = \sqrt{K_h}$ independent of 'c' initial concentration

Q The pH of 0.1 M NaCl at 90°C

(i) = 7
(ii) < 7
(iii) > 7
(iv) none of the above.

$\underset{SB}{Na}\underset{SA}{Cl}$ (Neutral solution).

At = 25°C pH = 7

At 90° pH = 6.

? Which of the following has highest pH ?

(I) $CuSO_4 \longrightarrow$ WBSA $pH < 7$
(II) $NaCl \longrightarrow$ Neutral $pH = 7$
(III) $NaCN \longrightarrow$ SBWA $(pH > 7)$
(iv) $CH_3COONH_4 \rightarrow$ WAWB (almost neutral $pH \simeq 7$)

Q Which of the following has highest pH?

(1) $LiCl \longrightarrow$ WBSA $pH < 7$
(II) $MgCl_2 \longrightarrow$ WBSA $pH < 7$
(III) $BaCl_2 \longrightarrow$ SBWA $pH > 7$
(iv) $CaCl_2 \longrightarrow$ WBSA $pH < 7$

Q Which of the following has more pH

(a) NaCN (b) Na_2CO_3.

Sol^n $pH = 7 + \frac{1}{2} pka + \frac{1}{2} \overset{\text{Same}}{\cancel{\log c}}$

$HCN \rightleftharpoons H^+ + CN^-$

$ka^1 = \frac{[CN^-][H^+]}{[HCN]}$

$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$

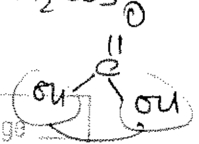
$ka^2 = \frac{[2H^+]^2 [CO_3^{2-}]}{[H_2CO_3]}$

$ka_2 > ka_1$

$pka_1 > pka_2$

So $pH = 7 + \frac{1}{2} pka$ So pH of NaCN is more.

H_2CO_3



Q $CN^- + H_2O \rightleftharpoons HCN + OH^-$

or

For anion hydrolysis which is correct.

(i) $h = \sqrt{K_h}$

(ii) $h = \sqrt{\frac{K_h}{C}}$

(iii) $[H^+] = \sqrt{\frac{K_w \times K_a}{C}}$

(iv) Both (ii) & (iii)

Anionic hydrolysis

WASB

$h = \sqrt{\frac{K_h}{C}}$

$[OH^-] = \sqrt{K_h \times C}$

$= \sqrt{\frac{K_w}{K_a} \times C}$

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

$[H^+] = \frac{K_w}{\sqrt{\frac{K_w}{K_a} \times C}}$

$= \sqrt{\frac{K_w \times K_a}{C}}$.

Q. 'X' is a salt when added in water its solution becomes twice alkaline than water find the nature of solution, type of salt and pH of solⁿ.

Solⁿ Solution = Basic $\left(\overset{\text{type}}{\text{WASB}}\right)$ salt

$[OH^-] = 2 \times 10^{-7}$

$pOH = 7 - \log 2$

$= 7 - 0.3 = 6.7$

$pH = 14 - 6.7$

$= 7.3$

Q. Calculate the pH of 0.1M CH_3COONa sol^n given ionisation const of CH_3COOH is $ka = 1.8\times10^{-5}$.

Sol^n

CH_3COONa

$\underset{WA}{\longleftrightarrow}\ \underset{SB}{\longleftrightarrow}$

$$\begin{array}{r} 5.00 \\ 0.26 \\ \hline 4.74 \end{array}$$

$$pH = 7 + \frac{1}{2}pka + \frac{1}{2}\log c$$

$$= 7 + \frac{1}{2}(5 - \log 1.8) + \frac{1}{2}\times(-1)$$

$$\begin{array}{r} 2.37 \\ 7.00 \\ 0.50 \\ \hline 9.87 \end{array}$$

$$= 7 + \frac{1}{2}(5 - 0.26) + (+\tfrac{1}{2})(-1)$$

$$7 + \frac{1}{2}\times 4.74 + \left(-\frac{1}{2}\right)$$

~~$= 7 + 2.37 + 0.5$~~

~~$= 9.87$~~

$$7 + \frac{1}{2}(5 - 0.26 - 1)$$

$$= 7 + 2.37 - 0.5$$

$$= 8.87$$

Note :- The Salt solution are either weakly acidic or weakly basic except that of SASB salt.

Q Arrange the pH in increasing order?

Sol^n

pH

0.1 M NaOH (I) → Strongly Basic

0.1 M NaCl (II) → Neutral

0.1 M HCl (III) → Strong Acidic

0.1 M NaCN (IV) → weakly basic.

0.1 M NH_4Cl (V) → weakly acidic

~~III > V > II > IV > I~~ . ③ < 5 < (II) < (IV) < (I)

$\overleftrightarrow{WB}$ SA

Q Calculate the hydrolysis const of NH_4Cl Given ionisation const of NH_4OH is 1.8×10^{-5}

$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} = \frac{1 \times \overset{5}{\cancel{10}}}{\underset{9}{\cancel{18}}} \times 10^{-14+5}$$

$$9\overline{)50}(0.55$$
$$45$$
$$5$$

$$= \frac{5}{9} \times 10^{-9}$$

$$= 0.55 \times 10^{-9}$$
$$= 5.5 \times 10^{-10}$$

Q Calculate the degree of hydrolysis of 0.1M NH_4CN given ionisation const of NH_4OH and HCN is 10^{-5} and 10^{-5} resp.

$$K_h = \frac{K_w}{K_a \times K_b} = \frac{10^{-14}}{10^{-5} \times 10^{-5}} = 10^{-14+10} = 10^{-4}$$

$$h = \sqrt{K_h} = \sqrt{10^{-4}} = 10^{-2}$$

$$h\% = 10^{-2} \times 100 = 1\%$$

Q Calculate the degree of hydrolysis $\frac{N}{100}$ NaCN if ionisation const of HCN is 1.4×10^{-9}

$$K_h = \frac{K_w}{K_a} =$$

$$h = \sqrt{K_h \times C} = \sqrt{\frac{K_w}{K_a} \times C}$$

$$h = 10^3 \times \frac{1}{\sqrt{14}}$$
$$= 10^3 \times \frac{1 \times \overset{2}{\cancel{10}}}{\cancel{3.7}\,7}$$

$$h = \sqrt{\frac{10^{-14+7}}{1.4}} \cdot \sqrt{\frac{10^{-7}}{1.4}} \qquad h = \sqrt{\frac{10^{-14}}{1.4 \times 10^{-9}} \times \frac{1}{100}}$$

$$h = 10^3 \times \frac{1}{\sqrt{\ldots}}$$

$$0.3 \times 10^3$$
$$= 3 \times 10^2$$

Soln $K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.4\times10^{-9}} = \frac{10^{-14+9}}{1.4} = \frac{10^{-5}}{1.4}$

$h = \sqrt{\frac{K_w}{K_a}\times\frac{1}{C}} = \sqrt{\frac{10^{-5}}{1.4}\frac{1}{\times\cancel{100}10^{-2}}}$

$= \sqrt{\frac{10^{-5+2}}{1.4}} = \sqrt{\frac{10^{-3}}{1.4}}$

$= \sqrt{\frac{10\times10^{-4}}{1.4}}$

$= 10^{-2}\sqrt{\frac{\cancel{10}\times10\ 80}{\cancel{14}\ 7}}$

$= \sqrt{7}\times10^{-2}$

$= 2.7\times10^{-2}$

Q Calculate the pH of 0.1M NaX soln given pKb of $X^- = 4.8$
(Note HX is a weak acid)

$\underset{SB\ \ WA}{NaX}$

pKa + pKb = 14
pKa = 14 − 4.8
= 9.2

$pH = 7 + \frac{1}{2}pKa + \frac{1}{2}\log c$

$= 7 + \frac{1}{2}\times9.2 + \frac{1}{2}(-1)$

$= 7 + \frac{1}{2}(9.2 - 1) = 7 + \frac{1}{\cancel{2}}(\overset{4.1}{\cancel{8.2}})$

$= 11.1$

Q When 0.1 M NH_4OH soln is mixed ~~mix~~ with 0.1 M CH_3COOH soln then calculate the pH of soln formed on mixing given ionisation const of CH_3COOH and NH_4OH is 10^{-5} and 10^{-7} resp.

Soln
Reacn

~~Kh~~ $pH = 7 + \frac{1}{2}pKa - \frac{1}{2}pKb$

$\underset{\substack{0.1M\\0}}{CH_3COOH} + \underset{\substack{0.1M\\0}}{NH_4OH} \rightarrow \underset{\substack{0\\ \underline{0.1M}}}{CH_3COONH_4} + H_2O$. (volume . ,

$= 7 + \frac{1}{2}(5 - 7) = 7 + \frac{1}{\cancel{2}}\times(-\cancel{2})$

pH = 6

H/W Pg-144
35-56
Pg 178 102, 103, 104,
133
Ex-2
Q 2, 4, 5,
7, 8, 9,
19, 23, 26, 28, 30, 32,
35

Neutralisation Reacⁿ (K_1) →

$$A + B \rightleftharpoons \text{salt} + \text{water}$$

← salt hydrolysis (k_h)

$$\boxed{K_1 = \frac{1}{k_h}}$$

Q. $CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$

($k_a = 10^{-5}$) $\quad K_{neutralisation}$

$$K_h = \frac{k_w}{k_a} = \frac{10^{-14}}{10^{-5}} = 10^{-9}$$

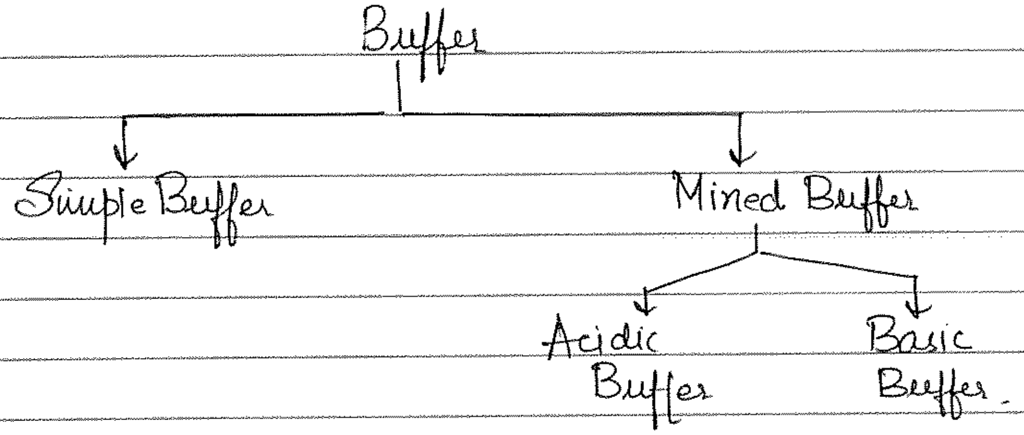
$$K_{neutralisation} = \frac{1}{k_h} = \frac{1}{10^{-9}} = 10^{9}$$

⇒ Buffer Solution :-

* A solution whose pH doesn't change significantly upon the addition of small amount of strong acid or strong base is known as buffer solution.

OR

* A sol^n whose pH almost remain constant is known as Buffer sol^n Or A sol^n which resist the change in pH is known as Buffer sol^n.



I. Simple Buffer :-

* aqueous sol^n of WAWB type salt

eg $CH_3COONH_4(aq)$, $NH_4CN(aq)$ $AgCN(aq)$, $HCOONH_4$, etc.

* pH of Solution :-

$$\boxed{pH = 7 + \frac{1}{2}pka - \frac{1}{2}pkb}$$

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→ Buffer Mechanism :-

$$CH_3COONH_4(aq) \longrightarrow CH_3COO^-(aq) + NH_4^+(aq)$$

$$\underset{(CB)}{CH_3COO^-} + \underset{(CA)}{NH_4^+} + H_2O \rightleftharpoons \underset{Acidic}{CH_3COOH} + \underset{Basic}{NH_4OH}.$$

When HCl is added :-

$$HCl \rightarrow H^+ + Cl^-$$

$$\left.\begin{array}{l} CH_3COO^- + H^+ \longrightarrow CH_3COOH \\ NH_4OH + H^+ \longrightarrow NH_4^+ + H_2O \end{array}\right\} H^+ \text{ is consumed.}$$

When NaOH is added.

$$NaOH \longrightarrow Na^+ + OH^-$$

$$\left.\begin{array}{l} NH_4^+ + OH^- \longrightarrow NH_4OH. \\ CH_3COOH + \cancel{H_3}OH^- \longrightarrow CH_3COO^- + H_2O \end{array}\right\} OH^- \text{ is consumed.}$$

(II) Acidic Buffer :-

* Aqueous solⁿ of weak acid and salt of same weak acid with any strong base. (salt = WASB)

Short form = WA + WASB salt.

eg $CH_3COOH + CH_3COONa$, $HCN + KCN$

or

$CH_3COOH + CH_3COOK$.

* Aqueous solⁿ of weak acid and its conjucate base .

eg = $\underset{WA}{CH_3COOH} + \underset{CB}{CH_3COO^-}$

$\underset{WA}{HCN} + \underset{CB}{CN^-}$.

⇒ Buffer Mechanism :-

$\underset{\text{Acidic.}}{CH_3COOH} + [\underset{C.B}{CH_3COO}]Na$

Hcl is added :-

$HCl \longrightarrow H^+ + Cl^-$

$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$ } H^+ is consumed .

When NaOH is added :-

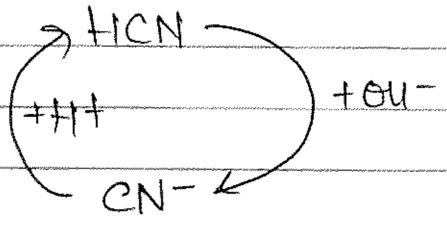
$NaOH \longrightarrow Na^+ + OH^-$

$CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$ } ~~wh~~ $\bar{OH}$ is consumed

* Hence value of pH almost const.

$$\begin{tikzcd}
CH_3COOH \arrow[d, bend left=60, "+OH^-"] \\
CH_3COO^- \arrow[u, bend left=60, "+H^+"]
\end{tikzcd}$$

eg HCN CN^-



⇒ **pH of acidic Buffer sol^n :-**

$$\boxed{pH = pka + \log \frac{[salt]}{[WA]}}$$

or

$$\boxed{pH = pka + \log \frac{[C.B]}{[Acid]}}$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

$c \quad 0 \quad 0$

$t=t_{eq} \quad 0 \quad ⓒ \quad c$

Here $[CH_3COONa] = [CH_3COO$

$[salt] = [CB]$

pka = − log ka .
[salt] = conc^n of salt in Normality
[C.B] = conc^n of conjucate base in normality .
[WA] = conc^n of weak acid in Normality

* pH of working range of Acidic Buffer :-

When $\frac{[salt]}{[weak\ acid]} = \frac{1}{10}$ to $\frac{10}{1}$ then does work

$$pH = pka + \log \frac{[salt]}{[water]}$$

$$\left.\begin{aligned} &= pka - 1 \\ &= pka + 1 \end{aligned}\right\}$$ For both above case .

pH working range = (pka − 1) to (pka + 1)

Max buffer action :-

When $\frac{[salt]}{[WA]} = \frac{1}{1}$ or $[Salt] = [WA]$

then Buffer works maximum

At $\boxed{pH = pka}$, Buffer works maximum

g :- CH_3COOH / CH_3COO^-

$\hookrightarrow ka = 10^{-5}$

$pka = 5$

Range of pH

$pH = (pka-1)$ to $(pka+1)$

Range 4 to 6.

Maximum work $pH_{max} = pka$
$= 5$.

At $pH = 8.8$ = Buffer will not work as not in range

At $pH = 4.3$ = } Buffer will work
$pH = 5$ = }

Ⅲ Basic Buffer :-

* aqueous solⁿ of weakbase and salt of same weak base with any strong Acid

* Short form (WB + WBSA) salt
NH_4OH

eg NH_4Cl , $NH_4OH + (NH_4)_2SO_4$

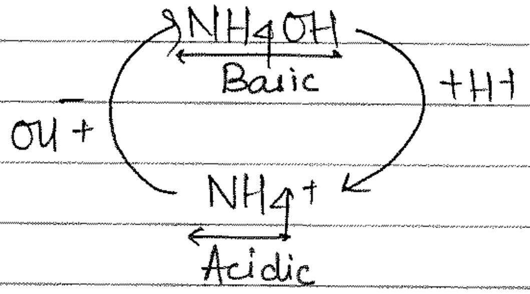
aqueous solⁿ of

* Weak base and its conjucate acid

$$\underbrace{NH_4OH}_{WB} / \underbrace{NH_4^+}_{CA}$$

* Buffer Mechanism :-

$NH_4OH + NH_4^+$



* pOH of Basic Buffer solⁿ :-

$$\left[pOH = pKb + \log \frac{[Salt]}{[WB]} \right]$$

$$pOH = pKb + \log \frac{[C.A]}{[WB]}$$

$pKb = -\log Kb$

[Salt] = concⁿ of salt in Normality

[WB] = concⁿ of Weak base in normality

[CA] = concⁿ of conjucate acid

* for working range of Basic Buffer :-

When $\frac{[salt]}{[WB]} = \frac{1}{10}$ to $\frac{10}{1}$ then Buffer does work.

for working range = (pkb-1) to (pkb+1)

* Maximum Buffer action when $\frac{[salt]}{[WB]} = \frac{1}{1}$ or [salt] = [WB]

then buffer does max work

$$\boxed{pOH_{max} = pkb}$$

⇒ Buffer capacity :-

* It measures the effectiveness of Buffer :-

* Larger the value of Buffer capacity more effective the buffer

* Buffer capacity = $\frac{\text{No of moles of SA or SB added per litre of sol}^n}{\text{change in pH}}$

Q 10 L sol^n 2mol HCl

pH → 4.1 to 4.09

$$\text{Buffer capacity} = \frac{\frac{2}{10}}{4.09 - 4.1} = \frac{2}{\cancel{10} \times (0.01)} \times 10\cancel{0}$$

$$= 20.$$

Note 1) pH of Buffer sol^n do not depend on dilution.

$$pH = pka + \log \frac{[salt]}{[Acid]}$$

$$= pka + \log \frac{n_{salt}/\cancel{V_{sol^n}}}{n_{WA}/\cancel{V_{sol^n}}}$$

(Hence independent

2) Blood = pH = 7.4

Buffer = H_2CO_3/HCO_3^-

(3) On dilution Buffer capacity of acidic or Basic buffer decreases

(4) Buffer solⁿ are solutions which have constant (reserve) acidity and basicity because the component of Buffer solⁿ react with SA or SB to form unionised acid or base

eg CH_3COOH / CH_3COO^-
when HCl is added
$CH_3COO^- + H^+ \longrightarrow CH_3COOH$ (non ionisable)

Q1. Which of the following will form Buffer ?

(i) $\overset{WA}{HCN} + \overset{CB}{CN^-} \longrightarrow$ ✓ (Acidic Buffer)

(ii) $\underset{WA}{HNO_2} + \underset{SBWA}{NaNO_2} \longrightarrow$ ✓ (Acidic Buffer)

(iii) $\underset{\text{Strong acid}}{HClO_4} + \underset{SASB}{KClO_4} \longrightarrow$ ✗

(iv) $\underset{WA}{H_3PO_4} + \underset{SBWA}{Na_3PO_4} \longrightarrow$ ✓ (Acidic Buffer)

(v) $\underset{WA}{H_2CO_3} + \underset{SBWA}{Na_2CO_3} \longrightarrow$ ✓ (Acidic Buffer)

(vi) $\underset{WA\ \ SB}{CH_3COONa}$ (aq) $\longrightarrow$ ✗

(vii) $\underset{WA\ \ WB}{CH_3COONH_4}$ (aq) $\longrightarrow$ ✓ (simple Buffer)

(viii) $\underset{\text{Aniline (Weak Base)}}{C_6H_5NH_2} / \underset{CA}{C_6H_5NH_3^+} \longrightarrow$ ✓ (Basic Buffer)

(ix) $\underset{2mol}{CH_3COOH} + \underset{1mol}{NaOH}$ }
$$\begin{array}{cccc} CH_3COOH & + NaOH & \longrightarrow & CH_3COONa + H_2O \\ 2mol & 1mol & & 0 \\ 1mol & 0\,mol & & 1mol \end{array}$$
Acidic Buffer

(x) $\underset{2mol}{CH_3COOH} + \underset{2mol}{NaOH}$ {
$$\begin{array}{cccc} CH_3COOH & + NaOH & \longrightarrow & CH_3COONa + H_2O \\ 2mol & 2mol & & 0 \quad\ 0 \\ 0 & 0 & & 2mol \end{array}$$
salt (salt

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(xi) $\underset{2\,mol}{HCl} + \underset{2\,mol}{NaOH}$ → Neutralization reacⁿ $HCl + NaOH \rightarrow \underset{\text{SASB}}{\underleftrightarrow{NaCl}} + H_2O$

(xii) $\underset{2\,mol}{HCl} + \underset{3\,mol}{NaCN} \longrightarrow$

$$\begin{array}{cccc} HCl & + NaCN & \longrightarrow & HCN + NaCl \\ 2\,mol & 5\,mol & & 0\,mol \\ 0 & 3\,mol & & 2\,mole \\ & \text{SBWA} & & \text{WA} \end{array}$$

SBWA — WA — Acidic Buffer.

(xiii) $C_5H_5N / \underset{\text{CA}}{\underleftrightarrow{C_5H_5NH^+}}$ → Basic Buffer

$\underset{\text{WB}}{\text{Pyridine}}$

Note:-

$WA + SB \longrightarrow WASB$

- $\rightarrow n_{WA} > n_{SB} \rightarrow$ Acidic Buffer
- $\rightarrow n_{moles\,WA} = n_{SB} \Rightarrow$ Salt Hydrolysis

$WB + SA \longrightarrow WBSA$

- $\rightarrow n_{WB} > n_{SA} \rightarrow$ Basic Buffers.
- $\rightarrow n_{WB} = n_{SA} \Rightarrow$ Salt Hydrolysis

(xiv) $\underset{\text{WB}}{\underleftrightarrow{NH_4OH}} + \underset{\text{WBSA}}{\underleftrightarrow{NH_4Cl}} \longrightarrow$ Basic Buffer.

(xv) $\underset{\text{WB SA}}{NH_4Cl} + \underset{\text{SB}}{\underleftrightarrow{NaOH}} \longrightarrow \underset{\text{WB}}{\underleftrightarrow{NH_4OH}} + NaCl$

← Basic Buffer $\left(n_{NH_4Cl} > n_{NaOH}\right)$

Date ______ Page ______

Acidic Buffer :-

HX / X^-

con^c = C_a C_s

$$\boxed{pH = pka + \log \frac{C_s}{C_a}}$$

$HX + X^-$

C_a, V_a C_s, V_s

$$[WA] = \frac{C_a V_a}{V_a + V_s}$$

$$[Salt] = \frac{C_s V_s}{V_a + V_s}$$

$$\boxed{pH = pka + \log \frac{C_s V_s}{C_a V_a}}$$

$$\boxed{pH = pka + \log \frac{\text{moles of salt / eq of salt}}{\text{moles of acid / eq of acid}}}$$

eg :-

Q

A B

CH_3COOH / CH_3COONa

0.1 M 0.2 M

0.2 M, 200 ml 0.4 M, 100 ml

2 mol 2 mol

3 eq 4 eq

$$pH = pka + \log \frac{0.2}{0.1}$$

$$= pka + \log \frac{0.4 \times 100}{0.2 \times 100}$$

$$= pka + \log \frac{2}{2}$$

$$= pka + \log \frac{4}{3}$$

Date ____ Page ____

Q Calulate the pH of basic buffer solⁿ having 0.2M NH_3 and 0.4 M NH_4^+ kb of NH_3 is 1.8×10^{-5}

$$\underbrace{\underset{WB}{NH_3} + \underset{CA}{NH_4^+}}_{\text{Basic buffer}}$$

$pka = -\log 1.8\times10^{-5}$

$= 5 - \log 1.8$

$= 5 - 0.27$

$= 4.74$

$$\begin{array}{r} 5.00 \\ 0.27 \\ \hline 4.73 \end{array}$$

$$\begin{array}{r} 4.74 \\ 0.30 \\ \hline 5.04 \end{array}$$

$$\begin{array}{r} 14.00 \\ 5.04 \\ \hline 8.96 \end{array}$$

$pOH = pkb + \log \frac{[0.4]}{[0.2]}$

$= 4.74 + \log 2$

$= 4.74 + 0.3$

$= 5.04$

$pH = 14 - 5.04 = 8.96$

$\simeq 9$

Q3 When 2N, 100ml acetic acid (CH_3COOH) is mixed with 4N, 50ml Sodium acetate (CH_3COONa) solⁿ then calculate the pH of solⁿ formed. Also calculate the conᶜ of H^+ ion in solⁿ ka $CH_3COOH = 1.8\times10^{-5}$

$pH = pka + \log \frac{[Salt]}{[Acid]}$ ← put equivalent

$pka = 5 - 1.8$

$= 4.74$

$$\begin{array}{r} 5.00 \\ 4.74 \\ \hline 0.26 \end{array}$$

$pH = 4.74 + \log \frac{[4\times\cancel{50}]}{[2\times\cancel{100}_{2}]}$

$pH = 4.74 + \cancel{\log 1}\ 0$ $(P_H = pka)$ $([H^+] = ka)$

$[H^+] = 10^{-4.74} = 10^{-5+0.26}$

$= 10^{+0.26}\times10^{-5}$

$= \cancel{2}\ 1.8\times10^{-5}$

14.00
9.26
$\overline{4.74}$

Q An acidic buffer solⁿ has equimolar conc of HA and A⁻ If pKb of A⁻ = 9.26. Calculate the pH

$$pH = pka + \log \frac{\cancel{[A^-]}}{\cancel{[HA]}} \xrightarrow{} 1 \text{(equimolar)}$$

$$pH = pka$$

$$pH = 4.74$$

$pka + pkb = 14$

$pka = 14 - 9.26$

$= 4.74$

Q. For an acidic Buffer solⁿ following relations is correct?

$$\frac{pH - pka}{2} = 1$$

which is correct.

(I) $[salt] = [WA]$

(II) $[salt] = 2[WA]$

(III) $[WA] = 2[salt]$

(IV) $[WA] = 100[salt]$

(V) None

$$pH = pka + \log \frac{[salt]}{[WA]}$$

Given

$$\frac{pH - pka}{2} = 1$$

$$pH = pka + 2$$

$$pH = pka + \log 10^2$$

$$pH = pka + \log \frac{\cancel{100}\, salt}{[WA]}$$

$$\cancel{WA} = \log 100 = \log \frac{salt}{[WA]}$$

$$[salt] = 100[WA]$$ ✓

2 In a basic Buffer solⁿ ratio of concⁿ of weak base to concⁿ of salt is increased upto 10 times. The pH of solⁿ is.

(i) increased by 2 unit   (iii) increased by 1 unit

(ii) decreased by 2 unit   (iv) Decreased by 1 unit.

$$\frac{[WB]}{[Salt]} \longrightarrow \frac{10[WB]}{[Salt]}$$

$$pOH = pkb + \log\frac{[salt]}{[WB]}$$

$$pOH_f = pkb + \log\frac{[Salt]}{[WB]}\times 10^{-1}$$

$$= pka + \log\frac{[salt]}{[WB]} + \log 10^{-1}$$

$$pOH = pka + \log\frac{[salt]}{WB} - 1$$

$$pH_i = 14 - pOH$$

$$pH_f = 14 - (pOH - 1)$$

$= 15 - pOH$ (~~Decrease~~ Increase by 1 unit)

Q Ka of HCOOH is 5×10^{-10} at 25°C for maintaing a pH of 9; what volume of 0.1M Sodium formate solⁿ must be added to 0.4M, 10 ml formic acid solⁿ

$$pH = pka + \log\frac{[Salt]}{[Acid]}$$

$$pka = 10 - \log 5$$
$$= 10 - 0.7$$
$$= 9.3$$

$$\begin{array}{r} 9.3 \\ 9.0 \\ \hline 0.3 \end{array}$$

$$9 = 9.3 + \log\frac{[0.1\times V]}{[0.4\times 10]}$$

$$-0.3 = \log\left[\frac{V}{40}\right]$$

$\text{Antilog} -0.3 = \overset{\text{antilog}}{\log}\left(\frac{V}{40}\right)$

$10^{-0.3} = \frac{V}{40}$

$10^{-1+0.7} = \frac{V}{40}$

$10^{-1} \times 10^{0.7} = \frac{V}{40}$

$5 \times 10^{-1} \times 40 = V$

$20\text{ ml} = V$

Q. Calculate the pH when (i) 60% of Formic acid is neutralised by KOH
(ii) Half of formic acid is neutralised by KOH
Ka of Formic acid $= 1.8 \times 10^{-5}$.

Sol^n WA + SB ⟶ WASB

$$HCOOH + KOH \longrightarrow HCOOK + H_2O$$

$t=0$ 100 moles 0 0 0

$t = t_{eq}$ 100−60 = 40 moles 60 moles

} assume 100 moles at t=0 (initial)

pKa = 5 − log 1.8
= 5 − 0.27
= 4.73

$$pH = pKa + \log\frac{[Salt]}{[WA]} =$$

$= 4.73 + \log\left[\frac{\cancel{60}}{\cancel{40}}\right]\frac{3}{2}$

$= 4.73 + (\log 3 - \log 2)$

$= 4.73 + (0.48 - 0.3)$

$= 4.73 + 0.18$

$= 4.91$

0.48
0.30
0.18
4.73
4.91

(II) $HCOOH + KOH \rightleftharpoons HCOOK + H_2O$

$t=0$ 100 mol $\quad 0 \quad 0$

$t=t_{eq}$ $100-50 \qquad 50$

$= 50$

$$pH = pka + \log \frac{[Salt]}{[WA]}$$

$$pH = 4.74 + \log \left[\frac{\cancel{50}}{\cancel{50}}\right]$$

$$pH = 4.74$$

Q. Calculate the pH when:-

① 0.2M, 100ml CH_3COOH is neutralised by 0.2M, 50ml NaOH

(II) 0.2M, 100ml CH_3COOH is neutralised by 0.2M, 100ml NaOH

ka of $CH_3COOH = 1.8 \times 10^{-5}$.

Sol

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O.$$

$t=0$ $\quad \frac{0.2 \times 1\cancel{00}}{10\cancel{00}} \quad \frac{0.2 \times \cancel{50}}{\cancel{1000}_2}$

$= \frac{0.2}{10} \quad \frac{0.2}{2}$

$= 20$ millimole $\quad {}^2 10$ millimole.

$t=t$ $\quad 10 \quad 0 \quad 10$

$$pH = pka + \log \frac{[salt]}{[WA]}$$

~~$= 4.74 + \log \left[\frac{\cancel{0.2} \times 50}{\cancel{0.2} \times \cancel{100}_2}\right]$~~

~~$4.74 + (\log 1 - \log 2)$~~

~~$= 4.74 - 0.3$~~

$= 4.74 + \log \frac{[10]}{[10]}$

$= 4.74$

4.74
0.30
4.44

Date ________ Page ____

(II) $CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$

0.2×100 0.2×100

$t=0$ $= 20$ mi   20 millimoles

$t = t_{eq}$ 0   0   20 millimoles.

$pH = 7 + \frac{1}{2} pKa + \frac{1}{2} \log C$

~~$= 7 + \frac{1}{2} \times 4.74 + \frac{1}{2} \times \log \left[\frac{0.2}{10}\right]$~~

~~$= 7 + \frac{1}{2}\left(4.74 + (\log 2 - \log 10)\right)$~~

~~$= 7 + \frac{1}{2}(4.74 - 0.7)$~~

~~$= 7 + \frac{1}{2}(4.04)$ 2.01~~

$$\begin{array}{r} 4.74 \\ 0.70 \\ \hline 4.04 \\ \hline \end{array} \qquad \begin{array}{r} 7.01 \\ 2.00 \\ \hline 9.01 \\ \hline \end{array}$$

$C = \frac{n_{salt}}{V_{solution}}$

$= \frac{20 \times 10^{-3} \times 10^{3}}{(100+100)}$

$= \frac{20}{200} = \frac{1}{10}$

$= 7 + \frac{1}{2}\left(4.74 + (\log 1 - \log 10)\right)$

$= 7 + \frac{1}{2}(4.74 - 1)$

$= 7 + \frac{1}{2} 3.74 = 7 + 1.87$

$= 8.87$.

$\frac{3.74}{2}$ 1.87

\# $CH_3COOH / (CH_3COO^-)Na^+$

a   s.

$pH = pKa + \log \frac{s}{a}$.

When HCl is added

CH_3COOH / CH_3COO^-.

$a + x$ $s - x$

$pH = pKa + \log \frac{s-x}{a+x}$

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

s x a.

$s-x$ 0 $a+x$

1. Calculate the pH of solⁿ having 0.2M CH_3COONa and 0.9M CH_3COOH If (1) 0.1M, 1ml HCl is added.

(2) 1ml of dilute HCl is added. pka = 4.74

(3) 0.1M, 1000ml HCl is added.

Volume of Buffer solⁿ is 1 (L).

solⁿ When HCl is not added.

$$pH = pka + \log\frac{[Salt]}{[WA]}$$

$$pH = 4.74 + \log\frac{[0.2]}{[0.9]}$$

$$= 4.74 + (\log 2 - \log 9)$$

$$= 4.74 + (-0.66)$$

$$= 4.08$$

(i) $nHCl = \frac{M \times Vml}{1000} = \frac{0.1 \times 1}{1000} = 10^{-4} mol$

When HCl is added in very less amount then pH remain const. pH = 4.08

(ii) pH = 4.08 (Because HCl is very much diluted hence pH remains const)

(iii) $nHCl = \frac{0.1 \times 1000}{1000} = 0.1 moles$

$$\underset{0.1 mol}{HCl} \longrightarrow \underset{0.1 mol}{H^+} + Cl^-$$

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

t=0   0.1   0.2   0.9

$$pH = pka + \log \frac{[Salt]}{[Acid]}$$

$$= 4.74 + \log \left[\frac{0.1}{1}\right]$$

$$= 4.74 + \log 1 - \log 10$$

$$= \underline{3.74}$$

AIIMS Syllabus

⇒ INDICATOR :-

* Indicator is a substance which changes its colour to detect the end points in acid base titration.

* Indicator are weak acid or weak base

* Indicator has two parts :-

(I) Ionised part (Dark colour)

(II) Unionised part (Light colour)

* Indicator changes it colour due to common ion or odd ion effect.

* Indicator

Acidic Indicator   Basic Indicator

(a) Acidic Indicator (HIn)

$$\underset{\text{(unionised part)}}{HIn} \rightleftharpoons \underset{\text{(Ionised part)}}{H^+ + In^-}$$

eg Phenophythalin $\underset{\text{Colourless}}{HPh} \rightleftharpoons \underset{\text{Pink}}{H^+ + Ph^-}$

* pH of acidic indicator

$$\boxed{pH = pK_{In} + \log\frac{[In^-]}{[HIn]}} = \frac{C.B/salt}{Weak\ acid}$$

$$pH = pK_{In} + \log\frac{[ionised]}{[unionised]}$$

* $pK_{In} = -\log K_{In}$

K_{In} = ionisation const of acidic indicator.

* pH working range of acidic Indictor :-

⇒ pH working range → $(pK_{In}-1)$ to $(pK_{In}+1)$

b) Basic Indicator (InOH)

$$\underset{(\text{unionised part})}{InOH} \rightleftharpoons \underset{(\text{Ionised part})}{In^+ + OH^-}$$

eg – Methyl orange

$$\underset{(\text{Yellow})}{MeOH} \rightleftharpoons \underset{(\text{Orange red})}{Me^+ + OH^-}$$

* pOH of basic indicator

$$\boxed{pOH = pK_{In} + \log\frac{[In^+]}{[InOH]}}$$

$pOH = pK_{In} + \log\frac{[Ionised]}{[unionised]}$ $\quad pK_{In} = -\log K_{In}$

rg 118 → 13~~4~~, 135, 137
138, 141, 142, 14
144, 145, 146, 14
151, 152, 153, 154, 1
– 169, 1
172

* pOH of working range :-

⇒ pOH range : $(pK_{In}-1)$ to $(pK_{In}+1)$

Indicator name	Acidic Medium	Basic Medium	pH working range
Methyl orange	orange red	Yellow	3.1 to 4.5 (orange Red) (Yellou
Methyl Red	Red	Yellow	4.2 to 6.2
Phenol Red	Yellow	Red	6.2 to 8.2
Phenopthylain	Colourless	Pink	8.2 to 10.2
Litmus	Red	Blue	5.5 to 8.3

TITRATION :-

* When acid is neutralised by base then their is sharp change in pH or sudden change in pH when equivalent point is about to come this sharp change or sudden change in pH is known as pH range of titration.

* That indicator is suitable whose pH working range lies b/w the pH range of titration.

* That equivalent point the equivalents of acid and base is equal though the nature of solⁿ may be acidic basic or neutral.

Tritration	pH range of titration	Suitable Indicator	Nature of sol^{n} at equivalent point
SA+SB	3-11	all	Neutral (pH=7)
SA + WB	3-7	Methyl orange Methyl Red	Acidic (PH<7)
WA+SB	7-11	Phenolpthalein	Basic (pH>7)
WA+WB	6.5-7.5	Phenol red.	Almost neutral

*Q Phenolpthalein is a suitable indicator for the titration of

1. $\underbrace{CH_3COOH}_{}$ + NaOH — $\overset{WA}{CH_3COOH} + \overset{SB}{NaOH}$
2. $NaOH + H_2SO_4 \longrightarrow SB+SA$
3. $HCl + KOH \longrightarrow SA+SB$
4. all.

Hence suitable for all.

Q. Calculate the pH of acidic indicator which is 20% unionised. Ionisation const of acidic indicator is 2×10^{-5}

[ionised] = 20% [unionised] = 80%.

$KIn = 2\times10^{-5}$

$pKIn = 5 - \log 2$

$= 5 - 0.3 = 4.7.$

$$pH = pKIn + \log\frac{[Ionised]}{[unionised]}$$

$= 4.7 + \log\frac{2\cancel{0}}{8\cancel{0}}$ $= 4.7 + (\log 1 - \log 4)$

$= 4.7 - 0.\cancel{60}$

$= \cancel{3.22} = 4.1$

4.70
0.~~06~~
3.22

4.7
0.6

Q Which indicator is siutable for the titration of $\underset{\text{WA (oxalic acid)}}{H_2C_2O_4}$ and $\underset{\text{(SB)}}{KOH}$

(1) Methyl orange
[✓ (2) phenolphatelin]
(3) Methy red
(4) all

(WASB) working range = 8.2 to 10.2

⇒ SOLUBILITY :- (S)

The maximum amount of solute that can be dissolved in a solvent to obtain 1 L of saturated solution at const temperature is known as solubility.

* Solubility is generally expressed in Molarity

$$\boxed{S = \frac{n_{solute}}{V_{solution}(L)} = \frac{m_{solute}}{M_{solute} \times V_{solution}(L)}}$$

Solubility in gram/L = Solubility × Molar mass

$$\boxed{S_{g/L} = S_M \times \text{Molar mass}}$$

Solubility product (ksp) :-

* When a sparingly soluble salt is added in water some part of it get dissolved and dissociate into ions such that an equilibrium is established b/w undissolved part and ionised part of salt.

that dissolves very less

$$AB_{(s)} \rightleftharpoons AB(aq)$$

$$AB(aq) \rightleftharpoons A^+_{(aq)} + B^-_{(aq)}$$

$$\underset{\text{undissolved}}{\boxed{AB(s)}} \underset{\text{precipitation}}{\overset{\text{Dissolution}}{\rightleftharpoons}} \underbrace{A^+ + B^-}_{\text{dissolved and ionised part}} \quad \Big\} \text{ saturated situation.}$$

$$\boxed{Ksp = [A^+][B^-]}$$

* ksp is defined for saturated solution only. (Because equilibrium is established)

* ksp is the product of con^c of ions in saturated sol^n with each raise to their power of their stichometric coefficient.

* Ksp depends only on temperature.

* Saturated sol^n is a sol^n in which there is eq/lmb b/w undissolved and ionised part of salt.

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eg $CaCl_2(s) \rightleftharpoons Ca^{2+}_{(aq)} + 2Cl^-_{(aq)}$

$ksp = [Ca^{2+}]^1 \times [Cl^-]^2$

$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$

$ksp = [Ca^{2+}]^3 \times [PO_4^{3-}]^2$

⇒ ksp in terms of solubility :-

eg $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

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

$t=t \quad a-S \qquad S \qquad S$

S = Solubility (Maxⁿ conᶜ that can be dissolved)

$ksp = [Ag^+] \times [Cl^-]$.

$ksp = S \times S$

$ksp = S^2$

eg $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$\qquad\qquad 2S \qquad S$.

$ksp = [Ag^+]^2 \times [CrO_4^{2-}]^1$

$= (2S)^2 \times (S)$

$= 4S^2 \times S \quad = 4S^3$.

For a general electrolyte :-

$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$

$$\boxed{ksp = x^x \cdot y^y \times S^{(x+y)}}$$

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2) 1. $Ag_2SO_{4(s)} \rightleftharpoons 2Ag^+ + SO_4^{2-}$

$Ksp = 2^2 \cdot 1^1 S^{(2+1)}$
$= 4S^3$.

2. $Al_2(SO_4)_3 \rightleftharpoons 2Al^{3+} + 3SO_4^{2-}$

$ksp = 2^2\, 3^3\, S^{(2+3)}$

$= 4 \times 9\, S^5$
$= 36\, S^5$

3. $NaKRbPO_4 \rightleftharpoons Na^+ + K^+ + Rb^+ + PO_4^{3-}$

$= 1^1 1^1 1^1 1^1 S^{(1+1+1+1)}$

$= S^4$

4. $Na_3Li_3(AlF_6)_2 \rightleftharpoons 8Na^+ + 3Li^{2+} + 2AlF_6^{-3}$

$= 3^3 \cdot 8^3 \cdot 2^2\, S^{(3+3+2)}$

$= 2727 \cdot 4\, S^8$

$= 27 \times 27 \times 4 \times S^8$

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Application of Solubility product (ksp):-

1. To find the Solubility :

(a) AB

eg Agcl, AgBr, CaSo4, Nacl, etc.

$$\boxed{ksp = S^2}$$

$$S = \sqrt{ksp}$$

(b) AB_2 or A_2B.

eg $Cacl_2$, Na_2S, etc.

$$\boxed{ksp = 4S^3} \qquad S = \left(\frac{ksp}{4}\right)^{1/3}.$$

(c) AB_3 or A_3B.

eg $Alcl_3$, Na_3Po_4

$$\boxed{ksp = 27S^4}$$

$$\left(\frac{ksp}{27}\right)^{1/4} = S$$

(d) A_2B_3 or A_3B_2.

eg $Al_2(So_4)_3$ or $Ca_3(Po_4)_3$

2
27
×4
108

$$ksp = 2^2 3^3 S^5$$

$$\boxed{ksp = 108S^5}$$

$$S = \left(\frac{ksp}{108}\right)^{1/8}$$

Ex-1 136, 134, 140
145, 146, 148,
149, 155, 170.

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Q. Calculate the ksp of As_2S_3 if solubility of As_2S_3 in its saturated solⁿ is 10^{-5} mol/dm³.

$\Rightarrow A_2B_3$ salt

1L = 1dm³ = 10^{-3} m³ = 10^3 cc = 10^3 cm³ = 10^3 mL

$$K_{sp} = 108\,S^5$$

$$= 108\,(10^{-5})^5$$

$$= 108 \times 10^{-25}$$

$$= 1.08 \times 10^{-23}$$

Q. Calculate the ksp of Ag_2SO_4 if concⁿ of Ag^+ ion in its saturated solⁿ is 4×10^{-3} M

$$K_{sp} = 4S^3$$

$$\underset{S}{Ag_2SO_4} \rightleftharpoons \underset{2S}{2Ag^+_{(aq)}} + \underset{S}{SO_{4\,(aq)}^{2-}}$$

$$2S = [Ag^+] = 4 \times 10^{-3}\ M$$

$$S = 2 \times 10^{-3}\ M$$

$$K_{sp} = 4 \times (2 \times 10^{-3})^3$$

$$= 4 \times 8 \times 10^{-9}$$

$$= 32 \times 10^{-9}$$

Date ______ Page ____

Q. Calculate the solubility product of Ag_2SO_4 at 25°c if the solubiuty Of Ag_2SO_4 in its saturated solⁿ is $2\times10^{-3}M$. also calculate the conc of Ag^+ & SO_4^{2-}

Solⁿ $Ag_2SO_4 \rightleftharpoons 2Ag^+ + SO_4^{2-}$

$2S \quad S$.

$[Ag^+] = 2\times2\times10^{-3}M$
$= 4\times10^{-3}M$

$[SO_4^{2-}] = 2\times10^{-3}$

$Ksp = 4S^3$.
$= 4\times(2\times10^{-3})^3$
$= 4\times8\times10^{-9} = 32\times10^{-9}$

Q. Calculate the pH of saturated solⁿ of $Ca(OH)_2$ if the solubility. product of $Ca(OH)_2$ is 4×10^{-9}

$Ksp = 4\times10^{-9}$.

$(ksp = 4s^3)$

$\cancel{4}s^3 = \cancel{4}\times10^{-9}$
$S = (10^{-9})^{1/3}$
$= 10^{-3}$.

$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$

$S \quad 2S$

$[OH^-] = 2\times10^{-3}$

$pOH = 3 - \log 2$
$= 3 - 0.3 = 2.7$

$pH = 14 - 2.7$
$= 11.3$

Date ______ Page ______

Q The solubility of AgCl is $1.435\ g/L$ Then calculate the solubility product of AgCl.

AgCl Mwt = 108 + 35.5
Mwt = 143.5 g

Mwt × S_M = $S_{g/L}$

$$S_M = \frac{1.4\cancel{35} \times 1\cancel{0}}{143\cancel{.5} \times 100\cancel{0}} = \frac{1}{100}$$

$$K_{sp} = S^2$$
$$= (10^{-2})^2 = 10^{-4}$$

$\Rightarrow$ $\boxed{\begin{array}{l} K_{sp}\uparrow \Rightarrow S\uparrow \\ K_{sp}\downarrow \Rightarrow S\downarrow \end{array} \text{(for same type of electrolyte)}}$

Q I Which salt is more soluble.

✓(i) CuS ($K_{sp} = 3 \times 10^{-11}$)
(ii) FeS ($K_{sp} = 4 \times 10^{-15}$)
(iii) ZnS ($K_{sp} = 6 \times 10^{-23}$)
(iv) PbS. ($K_{sp} = 2 \times 10^{-31}$)

* Same type of electrolyte so $K_{sp}\uparrow \Rightarrow S\uparrow$.

II (i) AgCl ($K_{sp} = 10^{-10}$)
(ii) $AlCl_3$ ($K_{sp} = 15 \times 10^{-12}$)
(iii) $BaCl_2$ ($K_{sp} = 5 \times 10^{-21}$)
(iv) PbS. ($K_{sp} = 2 \times 10^{-18}$)

* Different type of electrolyte.

Sol^n (i) $ksp = s^2$

$s = \sqrt{ksp} = \sqrt{10^{-10}} = 10^{-5}$

(ii) $ksp = 27s^4$

$S = \left(\frac{ksp}{27}\right)^{1/4} = \left(\frac{15 \times 10^{-12}}{27}\right)^{1/4} = \left(\frac{15}{27}\right)^{1/4} \times 10^{-3}$

(iii) $ksp = 4s^3$

$s^3 = \frac{ksp}{4} \Rightarrow \left(\frac{5 \times 10^{-21}}{4}\right)^{1/3} = S = \left(\frac{5}{4}\right)^{1/3} \times 10^{-7}$

(iv) $ksp = S^2$

$S = \sqrt{ksp} = \sqrt{2 \times 10^{-9}}$.

Hence $S = \left(\frac{15}{27}\right)^{-1/4} \times 10^{-3}$ is max so solubuity max.

Q If solubility for salt are same then find relation b/w their solubelty product

1. AB
2. AB_2
3. AB_3
4. A_2B

Q Calculate the volume of water required to dissolve 1g of $BaSO_4 \cdot 5H_2O$ so as to form saturated solⁿ? ksp of $BaSO_4 \cdot 5H_2O$ is 9x106.

$$\begin{array}{r} {}^{2}{}^{1} \\ 137 \\ 96 \\ 90 \\ \hline 323 \end{array}$$

Solⁿ

$$ksp = s^2$$

$$S = \sqrt{ksp} = \sqrt{9\times10^{-6}} = 3\times10^{-3}$$

$$S = \frac{m}{M \times V(L)}$$

$m = 1g$
Mwt = 323

$$3\times10^{-3} = \frac{1}{323 \times V(L)}$$

$$V = \frac{1}{323\times3\times10^{-3}} = \frac{1}{1000\times10^{-3}} = 1(L)$$

=> Effect of common ion on solubility :-

$$\begin{array}{ccccc} S_{\text{common ion}} & < & S_{\text{water}} & < & S_{\text{odd ion.}} \\ \downarrow & & \downarrow & & \downarrow \\ S' & & S & & S'' \end{array}$$

eg:- Solubility of AgCl in presence of 'C' NaCl solution?

$$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$$

S' $\quad$ S' $\quad$ $S' + C$ (Due to common ion effect)

$\simeq C$

$$NaCl \longrightarrow Na^+ + Cl^-$$

C $\quad$ C $\quad$ $C + S'$ (Due to common effect)

$\simeq C.$

$ksp = [Ag^+][Cl^-]$

$ksp = S' \times C$

$$\boxed{S' = \frac{ksp}{C}}$$

S' → of AgCl

ksp → of AgCl

C → of NaCl.

eg: Solubility of $CaCl_2$ in 'C' NaCl solⁿ

$CaCl_2 \rightleftharpoons Ca^{2+} + 2Cl^-$

$s' \quad s' \quad 2s'$

$2s' + c$

$\simeq c$

$NaCl \rightarrow Na^+ + Cl^-$

$c \quad c \quad c + 2s'$

$\simeq c$

$K_{sp} = [Ca^{2+}][Cl^-]^2$

$K_{sp} = s' \times c^2$

$$\left[s' = \frac{K_{sp}}{c^2} \right]$$

Q. Calculate the solubility of AgCl in 0.1M KCl solⁿ. If Max concⁿ of AgCl in water is 4×10^{-5}

$[AgCl] = 4 \times 10^{-5} = [Ag^+] = s$

$K_{sp} = s^2$

$K_{sp} = (4 \times 10^{-5})^2$

$= 16 \times 10^{-10}$.

In KCl $\rightarrow$ $(K_{sp} = c \times s')$

of AgCl.

$$\boxed{s' = \frac{K_{sp}}{c}} = \frac{16 \times 10^{-10}}{0.1}$$

$= 16 \times 10^{-9}$

Solubility of AgCl in KCl.

of KCl.

Q. Calculate the solubility of $CaCl_2$ in 0.01 M $Ca(OH)_2$ solⁿ ?
Ksp of $CaCl_2$ is 4×10^{-10}.

$$CaCl_2 \rightleftharpoons Ca^{2+} + 2Cl^- \qquad Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

$$S' \quad S' \quad 2S' \qquad\qquad C \quad C \quad 2C$$

$$S'+C$$
$$\simeq C$$

$$ksp = [Ca^{2+}][Cl^-]$$
$$= [C][2S]^2$$
$$[C][4S'^2]$$
$$ksp = C \times 4S^2$$
$$\frac{\cancel{4}\times10^{-10}}{0.01} = \cancel{4}S^2$$
$$\sqrt{10^{-8}} = S = 10^{-4}\,M$$

* $[CaCl_2] = \frac{[Cl^-]}{2}$

As $[CaCl_2] = S'$ & $\frac{[Cl^-]}{2} = \frac{2S'}{2} = S'$

Q. Arrange the solubility of AgCl in increasing order
(1) in water
(2) in 0.1M NaCl
(3) in 0.1M NH_3

$$\underset{\text{common Ion}}{ii} < \underset{\text{water}}{i} < \underset{\text{odd ion}}{iii}$$

$$\xrightarrow{S\uparrow}$$

In odd ion . $AgCl \rightleftharpoons Ag^+ + Cl^-$

$Ag^+ + 2NH_3 \longrightarrow Ag(NH_3)_2^+$

Q. In which of the following solubility of AgCl is maximum or minimum.

(1) water
(2) 0.1 M NaCl → $[Cl^-] = 0.1$
(3) 0.1 M $BaCl_2$ → $[Cl^-] = 0.2$
(3) 0.1 M $AlCl_3$ → $[Cl^-] = 0.3$

} if common ion conc^n ↑ solubility ↓

$$\left[1 > 2 > 3 > 4 \right]$$

III. Condition of precipitation :-

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

$$K_{sp} = [Ag^+]_e \times [Cl^-]_e$$
(solubility product)
(at equilibrium for saturated sol^n).

$$Q_{sp} = [Ag^+]_t \times [Cl^-]_t$$
(Ionic product)
I.P. or K_{IP}
(at any instant of time for any solution).

Case Ist $Q_{sp} < K_{sp}$

* unsaturated sol^n further more salt can be dissolved

Case IInd. $Q_{sp} = K_{sp}$

* Saturated sol^n.

Case IIInd. $Q_{sp} > K_{sp}$

* Supersaturated sol^n further precipitation of salt takes place.

Q In which of the following case. ~~The~~ does calcium fluoride (CaF_2) at to precipitate.

ksp of CaF_2 is 10^{-10} $\qquad$ $CaF_2 \rightarrow Ca^{2+} + 2F^-$

(i) $[Ca^{2+}] = 10^{-2}$ M $\qquad$ Qsp = ~~10^{-6}~~ $10^{-2} \times 10^{-8} = 10^{-10}$

$[F^-] = 10^{-4}$ M $\qquad$ Qsp = ksp

(ii) $[Ca^{2+}] = 10^{-3}$ M $\qquad$ Qsp = $10^{-3} \times 10^{-10} = 10^{-13}$ $\qquad$ Qsp < ksp

$[F^-] = 10^{-5}$ M

(iii) $[Ca^{2+}] = 10^{-4}$ M $\qquad$ Qsp = $10^{-4} \times 10^{-4} = 10^{-8}$ $\qquad$ Qsp > ksp

$[F^-] = 10^{-2}$ M

(iv) $[Ca^{2+}] = 10^{-5}$ M

$[F^-] = 10^{-3}$ M $\qquad$ Qsp = $10^{-5} \times 10^{-6} = 10^{-11}$ $\qquad$ Qsp < ksp.

(iii) precipate forms but (i) just begins to precipitate

Q Equal volume of 0.1 M Ca^{2+} solution is mixed with 2×10^{-5} M F^- solution. Does CaF_2 precipitate or not?

ksp (CaF_2) = 10^{-10}.

Ans. After mixing $\qquad$ $CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$

$$[Ca^{2+}] = \frac{0.1}{2} = \frac{1}{2} \times 10^{-1} \text{ M}$$

$$[F^-] = \frac{2 \times 10^{-5}}{2} = 10^{-5} \text{ M}$$

$$Qsp = [Ca^{2+}][F^-]^2$$

$$= \left(\frac{1}{2} \times 10^{-1}\right)\left[10^{-5}\right)^2$$

$$= \frac{1}{2} \times 10^{-1} \times 10^{-10} = \frac{1}{2} \times 10^{-11} = 5 \times 10^{-12}.$$

Qsp < ksp (no precipitation)

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Q. 0.01M NaCl, 1000ml is mixed with 10^{-3}M, 4000ml $AgNO_3$ Sol^n. Does ppt of AgCl takes place or not. ksp of AgCl is 10^{-5}.

Sol^n

After mixing :-

$NaCl \rightarrow Na^+ + Cl^-$ $$[Cl^-] = \frac{10^{-2} \times \cancel{1000}}{\cancel{5000}} = \frac{C_1V_1}{V_1+V_2}$$

$$= \frac{1}{5} \times 10^{-2}$$

$AgNO_3 \rightarrow Ag^+ NO_3^-$ $$[NO_3^-] = \frac{10^{-3} \times 4\cancel{000}}{\cancel{5000}} = [Ag^+]$$

$$= \frac{4}{5} \times 10^{-3}$$

$$Q_{sp}\ AgCl = \frac{1}{5 \times 1} \times 10^{-2} \times \frac{4}{5} \times 10^{-3} = \frac{4}{5 \times 5} \times 10^{-5}$$

$$= \frac{0.8}{5} \times 10^{-8}$$

$$= \frac{8}{5} \times 10^{-6}.$$

$Q_{sp} < k_{sp}$ (No ppt)

Q. Equal volume of 10^{-3}M NaCl is mixed with 10^{-2}M $CaCO_3$. Does Na_2CO_3 precipitate or not. $k_{sp}\ Na_2CO_3 = 2 \times 10^{-5}$

$Na_2CO_3 \rightleftharpoons 2Na + CO_3^{2-}$

$$[Na^+] = [Cl^-] = \frac{10^{-3}}{2} \qquad [CO_3^-] = \frac{10^{-2}}{2}.$$

$$Q_{sp} = \left(\frac{10^{-3}}{2}\right)^2 \times \left(\frac{10^{-2}}{2}\right) = \frac{10^{-6}}{4} \times \frac{10^{-2}}{2}$$

$$Q_{sp} = \frac{1}{8} \times 10^{-8}.$$

$Q_{sp} < k_{sp}$ (no ppt)

Q. At what concentration of Ag^+ does AgCl precipitate in a solution having 0.01M Cl^-

Ksp of AgCl = 10^{-10}

$K_{sp} \cancel{>} [Ag^+][Cl^-]$ $\qquad$ $\underline{K_{sp} < Q_{sp}}$

$10^{-10} \cancel{>} [Ag^+][Cl^-]$

$\frac{10^{-10}}{0.01} \times 100 \cancel{>} Ag^+$

$10^{-8} \cancel{>} Ag^+$

$[Ag^+] \cancel{>} 10^{-8}$ $\qquad$ Hence $[Ag^+] > 10^{-8}$.

Q. At what pH does $Mg(OH)_2$ begin to ppt

Ksp of $Mg(OH)_2$ is 4×10^{-12}

3rd

$K_{sp} < Q_{sp}$.

$$\underset{S}{Mg(OH)_2} \rightleftharpoons \underset{S}{Mg^{2+}} + \underset{2S}{2OH^-}$$

$K_{sp} = 4S^3$

$\cancel{4} \times 10^{-12} = \cancel{4}S^3$

$(10^{-12})^{1/3} = S$

$S = 10^{-4}$

$[OH^-] = 2 \times 10^{-4}$

$pOH = 4 - \log 2$
$= 4 - 0.3 = 3.7$.

$pH = 14 - 3.7$
$= 10.3$

Q At what pH does $Mg(OH)_2$ begin to ppt in 0.01 M Mg^{2+} sol^n. ksp of $Mg(OH)_2$ is 10^{-12}.

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$$

$$S' \qquad S' \qquad 2S'$$

$$(S'+0.01) \approx 0.01$$

$4S^3 = ksp$

$Mg^{2+} = 0.01 M$.

$ksp = (S'+C)(2S')^2$

$ksp = C \times (2S')^2$

$\sqrt{\frac{ksp}{4C}} = S'$

$\sqrt{\frac{10^{-12}}{4 \times 0.01}}$

$S' = \sqrt{\frac{10^{-10}}{4}}$

$= \frac{1}{2} \times 10^{-5}$

$[OH^-] = 2S'$

$= \frac{\cancel{2} \times 10^{-5}}{\cancel{2}}$

$pOH = -\log 10^{-5}$

$= 5$

$pH = 14 - 5$

$= 9$

⓸ precipitation of NaCl and soap :-

For NaCl :-

$$NaCl_{(s)} \rightleftharpoons Na^+ + Cl^-$$

Initially $Qsp = ksp$.

When HCl gas is passed.

$$HCl \longrightarrow H^+ + Cl^-$$

conc^n of Cl^- increases at it comes from SA

$$Qsp(NaCl)\uparrow = [Na^+][Cl^-]\uparrow$$

$$[Cl^-]\uparrow \Rightarrow Qsp\uparrow$$

$Qsp > ksp$ Hence ppt of NaCl takes place

Soap :-

Initially

$C_{17}H_{35}COONa_{(s)} \rightleftharpoons C_{17}H_{35}COO^-_{(aq)} + Na^+_{(aq)}$; $Qsp = ksp$.

When Nacl is added.

$$Nacl_{(aq)} \longrightarrow Na^+_{(aq)} + cl^-_{(aq)}$$

$$Qsp_{(soap)}\uparrow = [C_{17}H_{35}\text{-}COO^-][Na^+]\uparrow$$

$Qsp > ksp$ (Hence soap ppt)

⇒ Ksp of Mercurous chloride (Hg_2cl_2) and mercuric chloride ($Hgcl_2$) :-

$$Hg_2cl_{2(s)} \rightleftharpoons Hg_2^{2+} + 2cl^-$$

$$\text{Ⓢ} \quad S \quad 2S$$

$$ksp = [Hg_2^{2+}] \times [cl^-]^2$$
$$= 4S^3.$$

$$Hgcl_2 \rightleftharpoons Hg^{2+} + 2cl^-$$

$$\text{Ⓢ} \quad S \quad 2S.$$

$$ksp = [Hg^{2+}] \times [cl^-].$$

$$ksp = 4S^3.$$

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⇒ Group precipitation :-

Same type
lowest ksp ⇒ first precipitate.
Left to right ksp increases → ksp(↑)

Top to Bottom KSP increases

	Radical	Group Reagent
Group 1 ksp (least)	Ag^+, Hg^+ (Hg_2^{2+}), Pb^{2+} (आगे) (होगा) (प्रभात)	dil HCl. (कल)
Group Ⅱ A	Pb^{2+}, Cd^{2+}, Bi^{3+}, Cu^{2+}, Hg^{2+} पंजाबी कुड़ी Bhi Chandigarh की होगी	H_2S in acidic medi Student
Ⅱ B.	As^{3+}, Sb^{3+}, Sn^{2+}, Sn^{4+} आसमान सब सुना सुना.	
Group Ⅲ.	Al^{3+} Fe^{3+} Cr^{3+} Allen की Faculty करोड़ो मे	NH_4OH in prensce of NH_4C ek है Hydroxide.
Group Ⅳ	Mn^{2+} Co^{2+} Ni^{2+} Zn^{2+} मनमोहन की नी जाना	H_2S in Basic mediu Sonia के पास
Group Ⅴ	Ba^{2+} Sr^{2+} Ca^{2+}	$(NH_4)_2CO_3$ in presen of NH_4Cl.
Group 6 (ksp maximum)	Mg^{2+}.	NaH_2PO_4

⇒ Polyprotic Acid or Poly Basic acid :-

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$; ka_1

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$; ka_2

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$; ka_3

$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-}$ $\boxed{ka} = ka_1 \times ka_2 \times ka_3$

overall dissociation const.

$ka_1 > ka_2 \gg ka_3$ (because it is very diffcult to release H^+ from HPO_4^{2-} because 2-ve charge)

$pka_1 < pka_2 < pka_3$.

⇒ Polyacidic base :-

$Al(OH)_3 \rightleftharpoons Al(OH)_2^+ + OH^-$; kb_1

$Al(OH)_2^+ \rightleftharpoons Al(OH)^{+2} + OH^-$; kb_2

$Al(OH)^{+2} \rightleftharpoons Al^{3+} + OH^-$; kb_3

$Al(OH)_3 \rightleftharpoons 3OH^- + Al^{3+}$; kb

$\boxed{kb} = kb_1 \times kb_2 \times kb_3$.

Overall dissociation const

$kb_1 > kb_2 > kb_3$

$Pkb_1 < Pkb_2 < Pkb_3$

Ex-2 (all)
Ex-1 (57-98)

Q. $H_2X \rightleftharpoons H^+ + HX^-$; $ka_1 = 2\times10^{-4}$
$HX^- \rightleftharpoons H^+ + X^{2-}$; $ka_2 = 3\times10^{-8}$.

What is overall dissociation const of H_2X?

$$ka = ka_1 \times ka_2 .$$
$$= 2\times10^{-4} \times 3\times10^{-5}$$
$$= 6\times10^{-9}.$$

Q. Calculate the pH of $\frac{2}{3}\times10^{-4}$ M H_3X solⁿ?

First step dissociation = 100%
2nd step dissociation = 50%
3rd step dissociation is negligible.

Solⁿ

$$H_3X \rightleftharpoons H^+ + H_2X^-$$
$$H_2X^- \rightleftharpoons H^+ + HX^{2-}$$
$$HX^{2-} \rightleftharpoons H^+ + X^{3-}$$

Step 1

$$\begin{array}{lccc} & H_3X & \rightleftharpoons H^+ & + H_2X^- \\ t=0 & C & 0 & 0 \\ t=t & 0 & C & C \end{array}$$

(as 100% dissociation)

Step 2

$$\begin{array}{ccc} H_2X^- & \rightleftharpoons H^+ & + HX^{2-} \\ C & 0 & 0 \\ C/2 & C/2 & C/2 \end{array}$$

Step 3

$$\begin{array}{ccc} HX^{2-} & \rightleftharpoons H^+ & + X^{3-}. \\ C & 0 & 0 \\ C & 0 & 0 \end{array}$$

$$[H^+]_{total} = C + C/2 = \frac{3C}{2}$$
$$= \frac{\cancel{3}}{\cancel{2}} \times \frac{\cancel{2}}{\cancel{3}} \times 10^{-4} = 10^{-4}$$

pH = 4

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ACID BASE THEORY :-

① Arrhenious concept :-

Acid :- Substance which produce H^+ ion in aqueous solution is acid eg :- $HCl_{(aq)} \rightleftharpoons H^+ + Cl^-$

Base :- Substance which produce OH^- ion in aqueous solⁿ is base

eg : $NaOH_{(aq)} \longrightarrow Na^+ + OH^-$

② Bronsted Lowry concept :-

Acid :- The substance Which donate H^+ ion in any solvent is known as Bronsted lowry acid.

eg :- $$\underbrace{HCl}_{Acid} + \underbrace{H_2O}_{Base} \rightleftharpoons Cl^- + H_3O^+$$

eg :- $$\underbrace{HS^-}_{Acid} + \underbrace{H_2O}_{Base} \longrightarrow H_3O^+ + S^{2-}$$

Base :- Substance which accept H^+ ion in any solvent is known as Bronsted Lowry Base

$$\underbrace{NH_3}_{Base} + \underbrace{H_2O}_{Acid} \longrightarrow NH_4^+ + OH^-$$

* $\boxed{\text{Acid} \xrightarrow{-H^+} \text{Conjucate Base}}$.

eg $HCl \xrightarrow{-H^+} CB.\ (Cl^-)$

$H_2O \xrightarrow{-H^+} CB\ (OH^-)$

$N_3H. \xrightarrow{-H^+} C.B\ (N_3^-)$
(Hydrazoic acid)

$NH_4^+ \xrightarrow{-H^+} CB\ (NH_3)$

exception case :- If by removing answer not coming then add OH-

* $H^+ \xrightarrow{+OH^-} CB\ (H_2O)$

* $Zn(OH)^+ \xrightarrow{+OH^-} CB\ (Zn(OH)_2)$

* $\boxed{\text{Base} \xrightarrow{+H^+} \text{Conjucate Acid}}$.

eg $NH_3 \xrightarrow{+H^+} CA\ (NH_4^+)$

$H_2O \xrightarrow{+H^+} CA\ (H_3O^+)$

$HSO_4^- \xrightarrow{+H^+} CA\ (H_2SO_4)$

$CO_3^{2-} \xrightarrow{+H^+} CA\ (HCO_3^-)$

$OH^- \xrightarrow{+H^+} CA\ (H_2O)$

exception case— By removing OH-

$Zn(OH)_2 \xrightarrow{-OH^-} Zn(OH)^+$

* Water is amphiprotic or amphoteric

$$\begin{tikzcd} & CA\ (NH_4^+) \\ \boxed{NH_3} \arrow[ur, "+H^+"] \arrow[dr, "-H^+"'] & \\ & CB\ (NH,^-) \end{tikzcd}$$

$$\underset{\text{Base}}{HCOOH} + \underset{\text{Acid}}{HF} \rightleftharpoons \underset{\text{Acid}}{HCOOH_2^+} + \underset{\text{Base}}{F^-}$$ (Which is acid)

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* Strength of Acid & Base :-

cidic rength reases ↓

$HClO_4$	हकलो
HI	की आई
HBr	बारात
H_2SO_4	सब
HCl	कल
HNO_3	जहा कर
H_3O^+	आना
HSO_4^-	सब
H_3PO_4	Ponds वाले
HF	Facial
CH_3COOH	
H_2CO_3	को
H_2S	सर से
NH_4^+	नीचे तक
HCN	Clean करवाना
Phenol	Phenol मे है
H_2O	
ethanol	
NH_3	
Methane	
H_2	

eg :- $\underset{S[A]}{HCl} + \underset{S[B]}{H_2O} \rightleftharpoons \underset{W[A]}{H_3O^+} + \underset{W[B]}{Cl^-}$ (If One side strong then other side weak)

eg :- $\underset{W(A)}{CH_3COOH} + \underset{W(B)}{H_2O} \rightleftharpoons \underset{S(B)}{CH_3COO^-} + \underset{S(A)}{H_3O^+}$

(so becomes weak) (acidic solvent)

eg :- $\underset{WA}{HCl} + \underset{WB}{CH_3COOH} \rightleftharpoons \underset{SB}{Cl^-} + \cancel{H_3O^+}\ \underset{SA}{CH_3COOH_2^+}$

eg :- $\underset{SA}{CH_3COOH} + \underset{SB}{NH_3} \rightleftharpoons \underset{WB}{CH_3COO^-} + \underset{WA}{NH_4^+}$

(so strong acid) (Basic solvent)

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⇒ REDOX REACTION :-

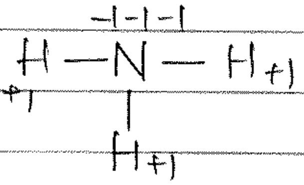
Reduction ⟶ gain of $e^{\ominus}$ or decrease in oxidation number

Oxidation ⟶ loss of $e^{\ominus}$ or increase in oxidation number

Oxidation number → It is the charge developed on an element due to electronegativity difference.

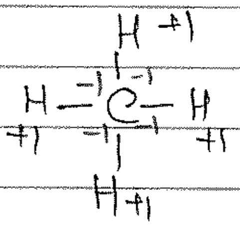
eg $\overset{}{\underset{+1}{H}}-\underset{-1}{Cl}$

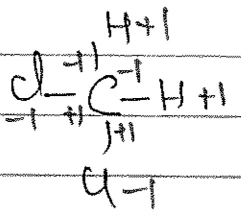
eg NH_3

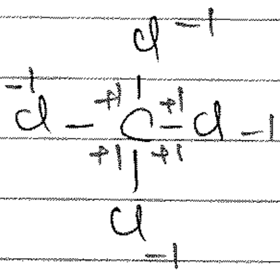


more en⊖ element ⟶ negative charge (−ve charge)
less en⊖ element ⟶ positive charge (+ve charge)

eg CH_4 CH_2Cl_2 CCl_4







'C' ON ⇒ −4 0 4

* Rules to determine the oxidation numbers :-

(1) covalent bond :

ⓐ Homoatomic molecule :-

$A-A$ $\quad$ $A=A$ $\quad$ $A\equiv A$

ON → 0 0 $\quad$ 0 0 $\quad$ 0 0

eg H_2 , O_2 , N_2

$H-H$ $\quad$ $O=O$ $\quad$ $N\equiv N$

ON → 0 0 $\quad$ 0 0 $\quad$ 0 0

ⓑ Heteroatomic molecule :- (Assume en⊖ B > A)

$A-B$ $\quad$ $A=B$ $\quad$ $A\equiv B$

+1 −1 $\quad$ +2 −2 $\quad$ +3 −3

eg $H-Cl$. $O=C=O$ $\quad$ $H-C\equiv N$

+1 −1 $\quad$ −2 +2,+2 −2 $\quad$ +1 −1,+3 −3

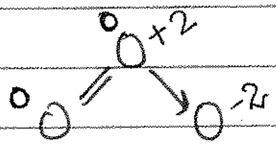
$\boxed{+4}$

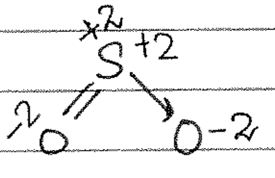
(2) Coordinate bond :-

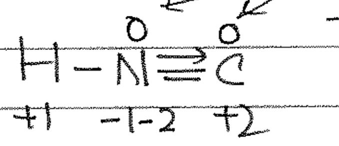
$A\longrightarrow A$ $\quad$ $A\rightarrow B$ $\quad$ $B\longrightarrow A$ $\quad$ {en⊖ B > en⊖ A}.

+2 −2 $\quad$ +2 −2 $\quad$ 0 0

eg O_3 $\quad$ SO_2 $\quad$ HNC (Hydrogen isocyanate)







'0' charge due to coordinate bond.

③ The sum of O.N of atoms of various element in a neutral molecule is zero and in charged species equal to charge present on it.

H_2SO_4

$+2 + x + 4(-2) = 0$

$x = +6$

CO_3^{2-}

$x + (-6) = -2$

$x = +4$

④ $O.N = 0$

(a) O.N of element in free state = 0

eg Na, Fe, Cl = 0

(b) O.N of element in homoatomic molecule = 0.

$O_2, H_2, N_2, P_4, S_8 = 0$.

(c) O.N in amalgum = 0

eg Na-Hg

ON = 0 0

(d) O.N in allotropes := 0.

C graphite, C diamond, Monoclinic S = 0.

(e) O.N of element in alloy = 0.

eg Brass

$\Downarrow$

Cu & Zn

0 0

(f) In glucose, fructose, sucrose O.N of 'C' = 0.

eg $C_6H_{12}O_6$.

$6x + \cancel{12} + (-\cancel{12}) = 0$

$x = 0$.

⑤ ON of fluorine is always −1

⑥ O.N of alkali and alkali earth metal is +1 and +2 respectively

IA → +1

IIA → +2

eg $NaCl$, $MgCl_2$

+1 +2

7) O.N of Hydrogen of hydrogen is generally +1 but in metal hydride is −1

eg H_2O, HCl, MgH_2, NaH

+1 +1 +2 −1 +1 −1

⑧ ON of O is generally = −2.

ⓐ peroxide ~~of~~ O = −1.

eg H_2O_2

$+2+2x=0$

$2x=-2$

$x=-1$

(O−O)

ⓑ superoxide

ON of O = $-1/2$

eg KO_2

$+1+2x$

$x=-1/2$

(c) Ozonide:

ON of O = $-1/3$.

eg KO_3

$+1+3x=0$

$x=-1/2$

⑧ Oxyfluoride. O·N of oxygen = +ve.

O_2F_2 , OF_2

$2x+(-2)=0$ $\quad$ $x+(-2)=0$

$x=+1$ $\quad$ $x=+2$

⑨

Max O·S	+4	+5	+5	+6	+2	+6	+7	+7	+8	+8
Element	C	P	N	S	O	Cr	Mn	Cl	Ru	Os
Min O·S	-4	-3	-3	-2	-2	0	0	-1	0	0

⑩ Charge of various species.

CN^-, OH^-, Cl^-, Br^-, NO_3^- (Charge = -1)

SO_4^{2-}, $C_2O_4^{2-}$ (Charge = -2)

PO_4^{3-}, AsO_4^{3-} (Charge = -3)

NH_3, H_2O, CO, C_2H_4 ⇒ (0 = charge)

NH_4^+, H^+, CH_3 (charge = +1)

Q. Determine the O.N. of underlined element in each case

① $\overset{+2}{H_2}\underline{C}\overset{(-6)}{O_3}$ $\quad x=4$

② $\overset{+1}{H}\underline{N}\overset{(-4)}{O_2}$ $\quad x=3$

③ $\overset{+1}{H}\underline{Cl}\overset{(-8)}{O_4}$ $\quad x=7$.

) $\overset{+1}{H}\underline{Cl}\overset{(-\cancel{6}8)}{O_3} = +5$

5) $\overset{(+3)}{H_3}\underline{P}\overset{(-8)}{O_4} = 5$

6) $\overset{+3}{H_3}\underline{P}\overset{(-4)}{O_2} = 1$.

7) $\overset{+1}{K}\underline{Mn}\overset{(-8)}{O_4} = +7$.

) $\overset{+2}{K_2}\underline{Cr_2}\overset{(-14)}{O_7}$ $n = +6$

) N_2H_4 $n = -2$

$2n + (-4)$

0) $X(C_2O_4)_2$ $n = +\cancel{2}4$

$(C_2O_4)^{2-}$

1) $\overset{+3}{Na_3}\underline{As}\overset{(-8)}{O_4}$ $n = 5$

2) $\overset{+1}{Li}Al\overset{\cancel{(+4)}}{H_4}$ Hydride $n = 3$.

$+1 + n + (-4)$

13) $\underline{Fe_2}O_3$ $2n + (-6) = 0$

$n = +3$.

14) $\underline{Mn}O_2$ $n = 4$

15) $\underline{N_3}H$ $3n + 1 = 0$

$n = -1/3$

MnO_4

$n + (-8) = 0$

No of peroxy oxygen $= 8 - 7$

$= 1 + 1$

$= 2$

$Mn O_4$

$n + (-2) + (-4) = 0$

$n = 6$

⑯ $\underline{N_2}H_4$

⑰ $Fe_{0.95}O$

$n \times (0.95) - 2 = 0$

$n = \frac{2 \times 100}{0.95} = \frac{200}{95}$

⑱ $\underline{Ni}(CO)_4$

$n + 4 \times 0 = 0$

⑲ $Ca\underline{OCl_2} \rightarrow Ca(OCl^-)(Cl^-)$

$-2 + n = -1$

$n = +1$

$n = -1$

⑳ $\underline{Fe_3}O_4 \Rightarrow FeO + Fe_2O_3$

$3n + (-8) = 0$ $\quad +2$ $\quad 2n + (-6) = 0$

$\boxed{n = 8/3}$ $\quad n = +3$.

㉑ $\underline{N}H_4\underline{N}O_3$

$n + (+4) = 1$ $\quad n + (-6) = -2$

$n = -3$ $\quad n = -2 + 6$

$n = +5$

㉒ CrO_5

$n + (-10) = 0$ $\quad$ No of PO $= 10 - 6$

$n = 10$ $\quad$ No of Po $= 4$

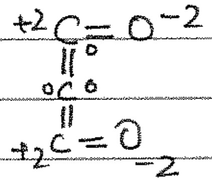
$n + (-4) + (-2) = 0$

$n = +6$

* ㉓ C_3O_2

$3n + 2(-2) = 0$

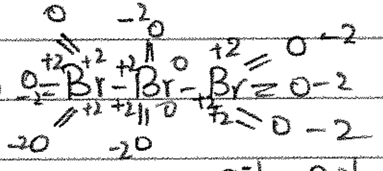
$n = 4/3$



* ㉔ $\underline{Br_3}O_8$

$3n + (-16) = 0$

$n = +16/3$

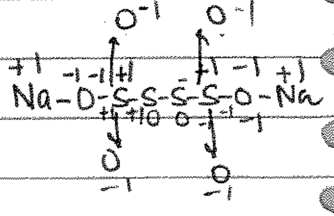


* ㉕ $Na_2\underline{S_4}O_6$

$2 + 4n + (-12) = 0$

$4n = 10$

$n = 2.5$



㉖ $Na_2\underline{S_2}O_3$

㉗ $H_2\underline{S}O_5$ (caro's acid)

㉘ $H_2\underline{S_2}O_7$ (Oleum)

㉙ $H_2\underline{S_2}O_3$ (Marshall's acid).

㉚ $H_4\underline{P_2}O_7$

㉛ $K_4\left[Fe(CN)_6\right]$

㉜ $Fe_3\left[Fe(Cl)_2(H_2O)(CN)_4\right]_2$

$Fe^{2+}\ \left[\underset{\downarrow}{Fe}(Cl)_2(H_2O)(CN)_4\right]^{3-}$

$x+(-2)+0+(-4)=-3$

$x=+3$

㉝ $(NH_4)_2SO_4$

$\underset{\downarrow}{N}H_4^{+}\ SO_4^{2-}$

$x+(+4)=+1$

$x=-3$

㉞ $Fe(NO_2)_2$

$Fe^{2+}\ (NO_2)^{-1}$

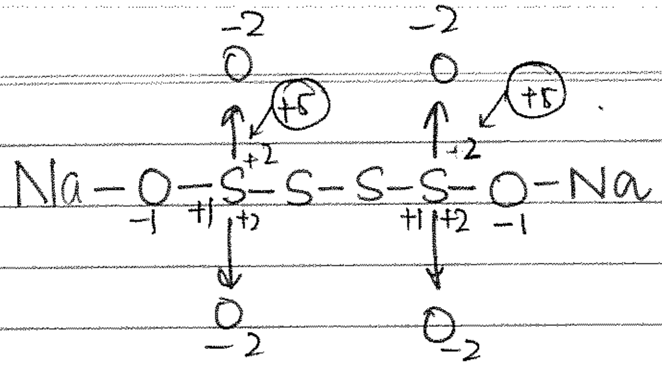
㉟ $FeSO_3$

$\downarrow$

Fe^{2+}

㉖ Mn_3O_4

$3x+(-8)=0 \quad x=+8/3$



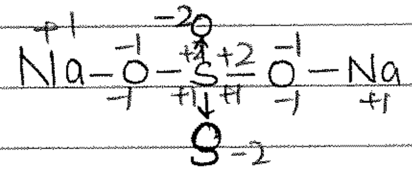
$Na-O-S-S-S-S-O-Na$

(26) $Na_2S_2O_3$

$2(+1)+2x+(-6)=0$

$2x=4$

$x=+2$



$S, S \rightarrow +6, -2$

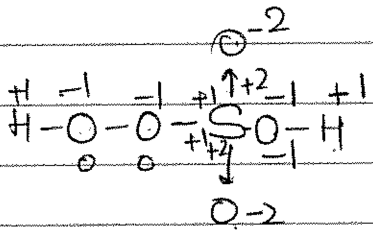
(27) H_2SO_5 No of peroxy oxygen

$+2+x+(-10)$ $= 8-6$

$x=8$ (✗) $= 2$

$+2+x+(-2)\times(-6)$

$\underline{\underline{x=+6}}$ ✓



(28) $H_2S_2O_7$

$(+2)+2x+(-14)=0$

$2x=12$

$x=+6$ O.N (of Both Sulphur)

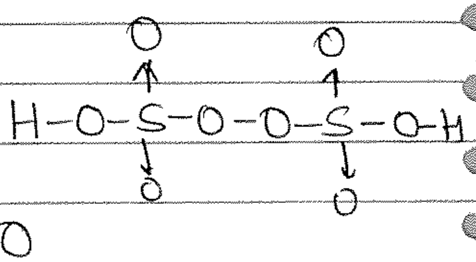
(29) $H_2S_2O_8$ No of peroxy oxygen.

$+2+2x+(-16)=0$ $= 7-6$

$2x=14$ $= 1+1 = 2$

$x=7$ $+2+2x+(-2)*(-12)=0$

$2x=12$



(30) $H_4P_2O_7$

$+4+2x+(-14)=0$

$2x=10$

$x=+5$

(31) $K_4[Fe(CN)_6]$

$[Fe(CN)_6]^{4-}$

$x+(-6)=-4$

$x=-4+6$

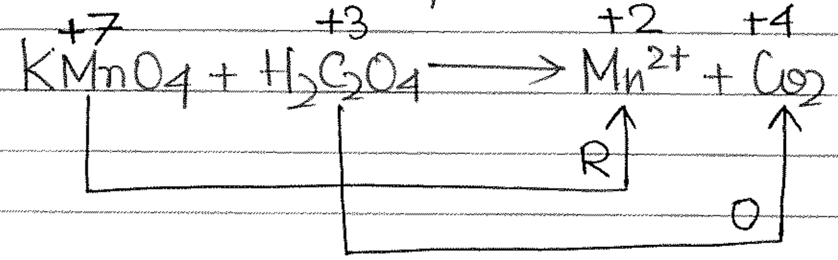
$x=2$

⇒ TYPES OF REDOX REACTION :-

① Intermolecular redox reac^n :-

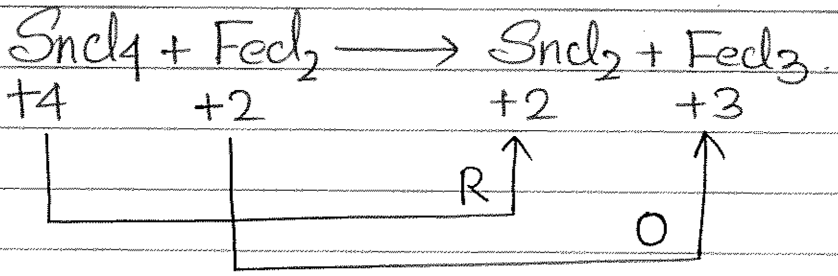
Reac^n in which oxidation and reduction of different elements in different compounds.

eg :-



$$K\overset{+7}{Mn}O_4 + H_2\overset{+3}{C_2}O_4 \longrightarrow \overset{+2}{Mn^{2+}} + \overset{+4}{CO_2}$$

eg :-

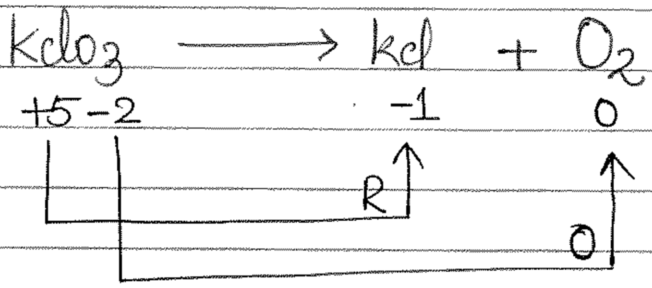


$$\underset{+4}{SnCl_4} + \underset{+2}{FeCl_2} \longrightarrow \underset{+2}{SnCl_2} + \underset{+3}{FeCl_3}$$

② Intramolecular redox reac^n :-

Reac^n in which oxidation and Reduction of different element in same compound

eg :-



$$\underset{+5\,-2}{KClO_3} \longrightarrow \underset{-1}{KCl} + \underset{0}{O_2}$$

3) Disproportionation reac^n :-

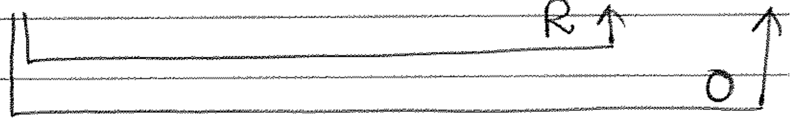
Reac^n in which oxidation and reduction of same element in same compound.

eg → $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$

-1 $\quad\quad -2 \quad 0$

eg → $Cl_2 + NaOH \longrightarrow NaCl + NaClO_3$

0 $\quad\quad +1\ -1 \quad +5$



⇒ Application of oxidation number :-

1) To compare acidic & Basic strength

Acidic nature ∝ oxidation number of central atom.

$$\text{Basic nature} \propto \frac{1}{\text{oxidation number}}$$

eg $HClO_4$, $HClO_3$, $HClO_2$, $HClO$.

$+7 \quad +5 \quad +3 \quad +1$.

Acidic strength $HClO_4 > HClO_3 > HClO_2 > HClO$.

eg HNO_2, HNO_3

$+1+x+(-4)$ $\quad +1+x+(-6)$ $\quad$ Acidic strength :- $HNO_3 > HNO_2$

$x=3$ $\quad x=+5$

Exception :-

H_3PO_4, H_3PO_3, H_3PO_2

$+5 \quad +3 \quad +1$

Real acidic order $H_3PO_2 > H_3PO_3 > H_3PO_4$

y $\underset{+1}{NaOH}$, $\underset{+2}{Ca(OH)_2}$, $\underset{+3}{Al(OH)_3}$

Basic strength $NaOH > Ca(OH)_2 > Al(OH)_3$

② To find molecular formula of compound :-
(By Hit & Trial method).

eg→ A compound has two elements X and Y such that their oxidation number is +1 and −2 respectively. Find the molecular formula of compound.

① $XY = +1+(-2) = -1$ (not zero)
② $XY_2 = +1+(-2)(-2) = -3$ (not zero)
③ $X_2Y = +1\times2+(-2) = 0$
④ X_3Y

③ To determine the oxidising and reducing agent.
(oxidant) (Reductant)

Oxidising agent ⟷ Reducing agent ⟷

$$\underset{+7}{KMnO_4} + \underset{+3}{H_2C_2O_4} \longrightarrow \underset{+2}{Mn^{+2}} + \underset{+4}{CO_2}$$

R O

Oxidising agent → → Substance which oxidise others and reduces themselves are OA
→ Their oxidation number decreases
→ They accepts / gain $e^{\ominus}$.
→ Compounds whose central atom is present in higher oxidation state act as oxidising agent.

eg $\underset{+7}{KMnO_4}$, $\underset{+6}{H_2SO_4}$, $\underset{+6}{K_2Cr_2O_7}$, $\underset{+5}{HNO_3}$, $\underset{+7}{HClO_4}$, etc.

Reducing agent → → Substance which reduces others and oxidise themselves are R.A.
→ Oxidation number increases.
→ They loss $e^{\ominus}$
→ Compounds whose central atom is present in lowest oxidation state act as reducing agent

eg $\underset{-1}{HCl}$, $\underset{-2}{H_2S}$, $\underset{-3}{NH_3}$

Note, H_2O_2 – act as both O.A and R.A

If the central atom has intermediate O.S then it can act as O.A as well as R.A eg H_2O_2, HNO_2, SO_2, etc.

1) To find the Equivalent wt of oxidising agent and reducing agent :-

$$Ewt = \frac{Mwt}{Vf}$$

n factor/vf = no of moles of $e^{\ominus}$ gain or lose by '1' mole of oxidation or Reductant

$vf = |a(x-y)|$ $\quad$ $x-y$ = change in O.N

a = no of atoms of elements

Case Ist → When only 1 atom in a given species changes its oxidation number

$$vf = |a(x-y)|$$

eg $\underset{+7}{KMnO_4} \longrightarrow \underset{+2}{Mn^{2+}}$ $\quad$ Change in ON = 5

$(x-y) = 5$

$a = 1$

$vf = 1 \times 5$

$Ewt_{KMnO_4} = \frac{M}{5}$

eg $C_2O_4^{2-} \longrightarrow CO_2$

$2x + (-8) = -2$

$2x = 6$

$x = +3$

$CO_2 \downarrow +4$

$x - y = 4 - 3 = 1$

$vf_{C_2O_4} = 2 \times 1 = 2$

$vf_{CO_2} = 1 \times 1 = 1$

$Ewt_{C_2O_4} = \frac{M}{2}$ $\quad$ $Ewt_{CO_2} = \frac{M}{1}$

eg $N_2 \longrightarrow NH_3$

$N_2 \downarrow 0$ $\quad$ $NH_3 \downarrow (-3)$

$x - y = 3$

$vf_{N_2} = 2 \times (+3) = 6$

$vf_{NH_3} = 1 \times 3 = 3$

$Ewt = \frac{M}{6}$ $\quad = M/3$

Case IInd → When more than one atom changes its oxidation number in an given species but either all increase or decrea

$vf = vf_1 + vf_2 + \ldots\ldots$

eg $\underset{+2\ +3}{FeC_2O_4} \longrightarrow \underset{+3}{Fe^{+3}} + \underset{+4}{CO_2}$

For Fe

$x - y = 1$

$vf\ Fe = 1 \times 1 = 1$

For C

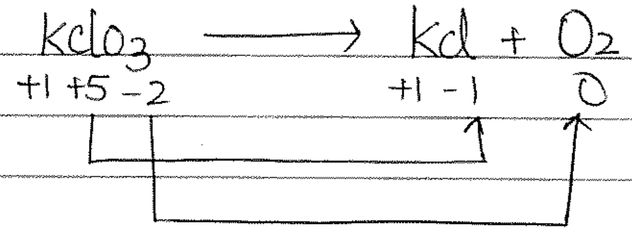
$x - y = 4 - 3 = 1$

$vf\ C_2 = 2 \times 1$
$= 2$

$vf\ FeC_2O_4 = 1 + 2 = 3$

Case IIIrd - When more than one atom changes its O.N in a given species

$vf = vf_1$ or vf_2



eg: $\underset{+1\ +5\ -2}{KClO_3} \longrightarrow \underset{+1\ -1}{KCl} + \underset{0}{O_2}$

For Cl

$vf = 1 \times (5 - (-1)) = 6$

For O

$vf = 3 \times (0 - (-2)) = 6$

vf for $KClO_3 = vf_1$ or vf_2
$= 6$

Case-IV :' Disproportionation Reac^n :-

$$\underset{0}{Br_2} \longrightarrow \underset{-1}{Br^-} + \underset{+5}{BrO_3^-}$$

R ↑   O ↑

Br_2 oxidation

$nf_1 = 2\times(\cancel{0}5-0)$
$= 10$

Br_2 reduction

$nf_1 = 2\times(0-(-1))$
$= 2$

n-factor Br_2 $nf = \dfrac{f_1f_2}{f_1+f_2} = \dfrac{10\times2}{10+2} = \dfrac{10\times\cancel{2}}{\cancel{12}\,6} = \dfrac{5}{3}$

Q. Calculate the n-factor in each case :-

(1) $\underset{-1}{I^-} \longrightarrow \underset{0}{I_2}$ $nf\ I^- = 1$ $nf\ I_2 = 2\times1$

(2) $IO_3^- \longrightarrow I^-$

$x+(-6) = -1$
$x = +5$ -1 . $nf_{IO_3} = 6$.

(3) $FeSO_4 \longrightarrow Fe_2O_3$

Fe^{2+} $2x+(-6) = 0$
$x = +3$.

$nf\ FeSO_4 = 1\times(3-2)$
$= 1$

$nf\ Fe_2O_3 = 2\times(3-2)$
$= 2$.

for NH_3 see here

(4) $N_2 + 3H_2 \longrightarrow 2\overset{+1}{NH_3}$

$0 \quad 0 \quad x+(3)=0$

$x=-3$

R ↑

0

$vf\ N_2 = 2\times(0-(-3))$
$= 6$

$vf\ H_2 = 2\times(1)$
$= 2$.

$vf\ NH_3$ from N $= 1\times 3 = 3$ | $vf\ NH_3$ from H $= 3\times(1)$
$= 3$.

(5) $Cu_2S \longrightarrow Cu^{2+} + SO_2$. (O.N of atom increases only)

$Cu^{+1}\ S^{2-}$ $\quad x+(-4)$, $x=4$

$+1 \quad (-2) \quad +2 \quad +4$

O↑ O↑

$vf\ Cu = 2(2-1)$.
$= 2$

$vf\ S = 1\times(4+2)$
$= 6$

$vf\ Cu_2S = 6+2$
$= 8$

(6) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr^{3+} + H_2O$.

$\downarrow$ 0 $\quad \downarrow$ +3

$NH_4^+ \quad Cr_2O_7^{2-}$

$x+(+4)=+1$ $\quad 2x+(-14)=-2$

$x=-3$ $\quad x=+6$.

$vf\ (NH_4)_2Cr_2O_7 = 6$

$vf\ N = 2\times(3) = 6$ $\quad vf\ Cr = 2\times(6-3) = 2\times 3 = 6$

7 $P_4 \longrightarrow PH_3 + H_3PO_4$

$0 \qquad -3 \qquad +3+n+(-8)=0$

$n=+5$

R↑ O↑

P_4 oxidation

$vf = 4\times(5) = 20$

P_4 reduction

$vf = 4\times(3) = 12$

$$vf\ P_4 = \frac{20\times12}{20+12} = \frac{\cancel{20}^{5}\times\cancel{12}^{3}}{\cancel{32}\,\cancel{8}\,2} = \frac{15}{2}$$

⑧ $FeO \longrightarrow Fe_2O_3$

$+2 \qquad +3$

$vf\ Fe_2O_3 = 2\times(3-2) = 2$ $\qquad vf\ FeO = 1\times(3-2) = 1$

Q Identify the redox reacⁿ

(1) $Cu_2S \longrightarrow Cu^{2+} + SO_2$

$+1 \quad (-2) \qquad +2 \qquad +4$

O↑ O↑

(2)✓ $KMnO_4 + C_2O_4^{2-} \longrightarrow Mn^{2+} + CO_2$

$+7 \qquad +3 \qquad +2 \qquad +4$

R↑ O↑

(3)✓ $Cl_2 \longrightarrow Cl^- + ClO_3^-$

$0 \qquad -1 \qquad n+(-6)=-1$

R↑ $\quad n=5$

O↑

(4) $NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O$

$+2+n+(-8) \qquad +2+n+(-8)$

$n=6 \qquad n=6.$

Date ______ Page ____

(5) $CaCO_3 \longrightarrow CaO + CO_2$

$+2+x+(-6)$ $\quad$ $+2\,(-2)$ $\quad$ $+4$

$x=4$

(6) ✓ $FeC_2O_4 + KMnO_4 \longrightarrow Fe^{3+} + CO_2 + Mn^{2+}$

$+2$ $\quad$ $2x+(-8)=-2$ $\quad$ $+7$ $\quad$ $+3$ $\quad$ $+4$ $\quad$ $+2$

$x=+3$

O $\quad$ R

O

→ BALANCING OF REDOX REAC$\underline{N}$:-

Ⓘ Ion electron Method :- given by Jaitley

Ⓘ Ⓘ Oxidation number method - given by Johnson.

Ⓘ Ion $e^{\ominus}$ method :-

eg :- $Fe^{2+} + MnO_4^- \xrightarrow{H^+} Mn^{2+} + Fe^{+3}$

$+2$ $\quad$ $+7$ $\quad$ $+2$ $\quad$ $+3$

R $\quad$ O

① Oxidation Half Reac$^{\underline{n}}$ $\qquad$ ⓘⓘ Reduction Half Reac$^{\underline{n}}$

$Fe^{2+} \longrightarrow Fe^{+3} + e^-$ $\qquad$ $8H^+ + MnO_4^- + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

charge $\quad 8+(-1)$ $\qquad$ $+2$.

$= 7$

Diff $= 7-2$

$= 5$

① × ⑤ + ⓘⓘ × 1.

$5Fe^{2+} \longrightarrow 5Fe^{3+} + 5e^-$

$\underline{5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O}$.

$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

eg:- $Cr_2O_7^{2-} + C_2O_4^{2-} \xrightarrow{H^+} Cr^{3+} + CO_2$

+6 +3 +3 +4

R↑ O↑

Date ______ Page ______

Oxidation Half Reacⁿ	Reduction Half Reacⁿ
~~Cr_2O_7~~ $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$	$14H^+ + Cr_2O_7^{2-} + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$
Total charge −2 0	Charge = 14−2 = 12 6 6
	Net charge = 12−6 = 6

(I) × 3 + (II) × 1

$3C_2O_4^{2-} \longrightarrow 6CO_2 + \cancel{6e^-}$

$14H^+ + Cr_2O_7^{2-} + \cancel{6e^-} \longrightarrow 2Cr^{3+} + 7H_2O$.

$14H^+ + 3C_2O_4^{2-} + Cr_2O_7^{2-} \longrightarrow 6CO_2 + 2Cr^{3+} + 7H_2O$,

eg:- $Zn + NO_3^- \longrightarrow NH_4^+ + Zn^{2+}$

0 5 $n + 4 = +1$ 2

$n = -3$

R↑ O↑

Oxidation Half Reacⁿ	Reduction Half Reacⁿ
$Zn \longrightarrow Zn^{2+} + 2e^-$	$10H^+ + NO_3^- + 8e^- \longrightarrow NH_4^+ + 3H_2O$
harge = 0 +2	Charge = 10−1 = 9 <1

Net charge = 8

(I) × 4 + (II) × 1

$4Zn \longrightarrow 4Zn^{2+} + \cancel{8e^-}$

$10H^+ + NO_3^- + \cancel{8e^-} \longrightarrow NH_4^+ + 3H_2O$

$10H^+ + 4Zn + NO_3^- \longrightarrow 4Zn^{2+} + NH_4^+ + 3H_2O$.

eg:- $Br_2 \xrightarrow{OH^-} Br^- + BrO_3^-$

$\overset{0}{}$ $\quad$ R $\overset{-1}{}$ $\quad$ O $\overset{+5}{}$

Oxidation Half Reacⁿ $\qquad\qquad$ Reduction Half Reacⁿ

$6H_2O + Br_2 \longrightarrow 2BrO_3^- + 12H^+ + 10e^-$ $\qquad$ $2e^- + Br_2 \longrightarrow 2Br^-$

$0 \qquad +5 \qquad +10e^-$ $\qquad\qquad$ $0 \qquad -2$

Total charge $= \cancel{16}-1 = 12-2$ $\qquad$ Total charge $= 2e$

$\qquad = 5 \quad = 10e^-$

~~(I) × 1 + (II) × 5 H~~

(I) × 1 + (II) × 5

$6H_2O + Br_2 \longrightarrow 2BrO_3^- + 12H^+ + \cancel{10e^-}$

$\cancel{10e^-} + 5Br_2 \longrightarrow 10Br^-$

$6H_2O + 6Br_2 \longrightarrow 2BrO_3^- + 12H^+ + 10Br^-$

$3H_2O + 3Br_2 \longrightarrow BrO_3^- + 6H^+ + 5Br^-$

For Basic medium Add OH⁻ both sides equal to no of H⁺ ions.

$3Br_2 + 3H_2O + 6OH^- \longrightarrow BrO_3^- + 5Br^- + 6H^+ + 6OH^-$

$3Br_2 + 3H_2O + 6OH^- \longrightarrow BrO_3^- + 5Br^- + 6H_2O$.

$3Br_2 + 6OH^- \longrightarrow BrO_3^- + 5Br^- + 3H_2O$.

IInd Oxidation number Method :-

eg $MnO_4^- + Fe^{2+} \xrightarrow{H^+} Mn^{2+} + Fe^{3+}$

O.N $\quad +7 \quad +2 \quad +2 \quad +3$

$vf_{Mn} = 7-2 = \boxed{5}_{\times 1}$ $\quad vf_{Fe} = 3-2 = \boxed{1}_{\times 5}$ } so that vf = equal.

$\underbrace{\quad}$ Multiply the reac^n by coeff i.e 5

$8H^+ + MnO_4^- + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$.

p

eg $Cr_2O_7^{2-} + C_2O_4^{2} \xrightarrow{H^+} Cr^{3+} + CO_2$

O.N $\quad +6 \quad +3 \quad +3 \quad +4$

$vf_{Cr} = (6-3)2 = \boxed{6}_{\times 1}$ $\quad vf_{C} = 2\times(4-3) = \boxed{2}_{\times 3}$. $\quad 6e^{\ominus}$ = no of ~~rec~~ $e^{\ominus}$ transfer in this redox reac^n

$\left(\cancel{10H^+} + Cr_2O_7^{2-} + 3C_2O_4^{2-} \xrightarrow{\cancel{H^+}} 2Cr^{3+} + 2\times3CO_2 + \cancel{5H_2O} \right.$
$\left. 1H_2O \qquad\qquad\qquad\qquad +2H^+ \right)$

Balance element other than H & O.

$Cr_2O_7^{2-} + 3C_2O_4^{2} \longrightarrow 2Cr^{3} + 2\times3CO_2$

Balance O.

$Cr_2O_7^{2-} + 3C_2O_4^{2} \longrightarrow 2Cr^{3+} + 6CO_2 + 7H_2O$

Balance H+

Balanced eq^n $\longrightarrow 14H^+ + Cr_2O_7^{2-} + 3C_2O_4^{2-} \longrightarrow 2Cr^{3+} + 6CO_2 + 7H_2O$

$x = 5$
$x = -1+6$
$x+(-6) = -1$

$x = -3$
$x = +1-4$
$x+(+4) = +1$

eg (3) :- $Zn + NO_3^- \xrightarrow{H^+} Zn^{2+} + NH_4^+$.

O.N 0 $+5$ $+2$ -3

vf Zn = 2 vf N = (5+3)

$② \times 4$ $= ⑧ \times 1$

$10H^+ + 4Zn + NO_3^- \xrightarrow{H^+} 4Zn^{2+} + NH_4^+ + 3H_2O$

$x+(-8) = -2$

eg (4) $Cr(OH)_3 + IO_3^- \xrightarrow{OH^-} CrO_4^{2-} + I^-$

O.N $+3$ $+5$ $+6$ -1

vf Cr vf I = (5+1)

$= ③ \times 2$ $= ⑥ \times 1$

$2Cr(OH)_3 + IO_3^- \xrightarrow{OH^-} 2CrO_4^{2-} + I^-$

Balance oxygen & H

~~4H~~ $+ 2Cr(OH)_3 + IO_3^- \xrightarrow{OH^-} 2CrO_4^{2} + I^- + H_2O$.
$+4H^+$

Balancing OH⊖ By adding equal amount of OH- equal to H+ both sides

$4OH^+ + 2Cr(OH)_3 + IO_3^- \xrightarrow{OH^-} + 2CrO_4^{2-} + I^- + H_2O + 4H_2O$

$4OH^- + 2Cr(OH)_3 + IO_3^- \xrightarrow{OH^-} 2CrO_4^{2-} + I^- + 5H_2O$

Q. Balance the half reacⁿ :-

$e^- + H^+ + NO_3^- \longrightarrow N_2 + H_2O$

$12H^+ + 2NO_3^- \longrightarrow N_2 + 6H_2O$

O.N +5 +10e⁻ 0 .

charge = 12 − 2
= 10 .

$12H^+ + 2NO_3^- + 10e^- \longrightarrow N_2 + 6H_2O$

Some important changes :-

① MnO_4^- (+7)

$\xrightarrow{\text{acidic}}$ Mn^{+2} vf = 5

$\xrightarrow[\text{or weakly basic}]{\text{neutral}}$ Mn^{+4} vf = 3

$\xrightarrow[\text{strongly}]{\text{Basic}}$ Mn^{+6} vf = 1 .

② If only alkaline written → weakly alkaline → Neutral.

③ $Cr_2O_7^{2-} \xrightarrow{\text{acidic}} Cr^{+3}$

+6 +3

$vf_{Cr_2O_7} = 2(6-3) = 6$.

④ $C_2O_4^{2-} \longrightarrow CO_2$

+3 +4

$vf_{C_2O_4} = 2\times(4-3) = 2$

⑤ $Fe^{+2} \longrightarrow Fe^{+3}$

$vf_{Fe} = 3-2 = 1$

(O.N of both increases)

⑤ $FeC_2O_4 \longrightarrow Fe^{+3} + CO_2$

$+2 \quad +3 \qquad\qquad +3 \qquad +4$

$vf_{Fe} = 3-2 = 1$

$vf_{C_2O_4} = (4-3) \times 2 = 2$

$vf_{FeC_2O_4} = 3$ (v

⑥ $H_2O_2 \xrightarrow{\text{oxidation}} O_2$ $\quad vf_{H_2O_2} = 2 \times (1) = 2$

$-1 \qquad\qquad 0$

$H_2O_2 \xrightarrow{\text{Reduction}} H_2O$.

$-1 \qquad\qquad (-2)$ $\quad vf_{H_2O_2} = 2(-1+2) = 2$

⑦ ~~IO_3^-~~ $\quad I^- \xrightarrow[\text{Medium}]{\text{Basic}} IO_3^-$ $\quad vf = (5-(-1)) = 6$

$-1 \qquad\qquad +5$

⇒ <u>Law of Equivalence</u> :-

$aA + bB \longrightarrow cC + dD$

$geq_A = geq_B = geq_C = geq_D$

$$\boxed{\begin{array}{l} \text{gram equivalent } (geq) = N \times V \\ geq = \text{moles} \times n\text{ factor} \end{array}}$$

Q Calculate the moles of $KMnO_4$ required to oxidise 2mole of FeC_2O_4 (Ferrous oxlate) in acidic medium.

$$\overset{+7}{KMnO_4} + FeC_2O_4 \xrightarrow{H^+} Mn^{2+} + Fe^{3+} + CO_2$$

v_f $KMnO_4$ = 7-2 = 5 $\quad$ v_f FeC_2O_4 = 3

$$\underset{n}{KMnO_4} + \underset{2mole}{Fe_2CO_4} \longrightarrow \text{Product}.$$

By law of equivalence geq $KMnO_4$ = geq Fe_2CO_4

$n \times 5 = 2 \times 3$

$n = \frac{6}{5}$ moles required of $KMnO_4$.

Q Calculate the moles of $KMnO_4$ required to oxidise 2mole KI in basic Medium. (consider weakly basic)

$$\underset{+7}{KMnO_4} + \underset{-1}{KI} \xrightarrow{OH^-} Mn^{+4} + \underset{+5}{IO_3^-}$$

v_f $KMnO_4$ = 3 $\quad$ v_f KI = 6.

$$KMnO_4 + KI \longrightarrow \text{Product}$$

$n \times 3 = 6 \times 2$

$n = \frac{6 \times 2}{3} = 4$ moles

Q Calculate the moles of dichromate required to oxidise 3mole of Cu_2S

$$Cr_2O_7^{2-} + Cu_2S \longrightarrow Cr^{3+} + Cu^{+2} + SO_2$$

Sol^n

$$\underset{+6}{Cr_2O_7^{2-}} + \underset{+1\ -2}{Cu_2S} \longrightarrow \underset{+3}{Cr^{3+}} + \underset{+2}{Cu^{+2}} + SO_2$$

$x + (-4) = 0$

$x = 4$.

$vf\ Cr_2O_7^{2-} = 2(6-3)$
$= 6$

$vf\ Cu_2S = vf\ Cu + vf\ S$
$= (2-1)\times 2 + (4+2)\times 1$
$= 2 + 6$
$= 8$.

$Cr_2O_7^{2-} + Cu_2S \longrightarrow$ Product.

$n \times 6 = 3 \times 8$.

$n = \frac{\cancel{3}\times\cancel{8}}{\cancel{6}\,\cancel{2}} = 4$ moles.

Q. In which of the following Least moles of $KMnO_4$ is required to oxidise equal moles of $FeSO_4$ and FeC_2O_4 in acidic medium.

Sol^n

$$\overset{+7}{KMnO_4} + \overset{+2}{FeSO_4} \longrightarrow Fe^{+3} + Mn^{+2}$$

$vf\ KMnO_4 = 5$ $\quad vf\ FeSO_4 = 3-2$
$= 1$.

(Leat $FeSO_4$ assume more = 1)

$5n = 1 \times 1$

$n = 1/5$

$$KMnO_4 + FeC_2O_4 \longrightarrow Fe^{+3} + CO_2 + Mn^{2+}$$

$vf\ KMnO_4 = 5$ $\quad vf\ FeC_2O_4 = 1 + 2$
$= 3$.

(Let FeC_2O_4 assume more = 1)

$5n = 1 \times 3$

$n = \frac{3}{5}$

Hence less moles of ~~Fe~~ $KMnO_4$ in oxidation of $FeSO_4$

complete
Ex-1,2,3

* Oxidising powes Of $KMnO_4$

acidic > Neutral or alkaline > strongly alkaline

* ~~Oxidation~~ oxidising power $\propto$ O.N

* $\underset{+7}{KMnO_4}$ has more oxidising power then $\underset{+6}{K_2Cr_2O_7}$.

* O.N of Fe in haemoglobin is +2

* $CuSO_4$ electrolyses $Cu^{2+} + SO_4^{2-}$.

vf $CuSO_4 = 2$ (Total +ve charge / Total −ve charge).

$$\underset{+2}{CuSO_4} + \underset{-1}{KI} \longrightarrow \underset{+1\ -1}{Cu_2I_2} + \underset{0}{I_2}$$

vf $CuSO_4 = (2-1)$
$= 2$

vf $I_2 = 2\times(1)$
$= 2$

vf $KI = 1\times(0(-1))$
$= 1$.