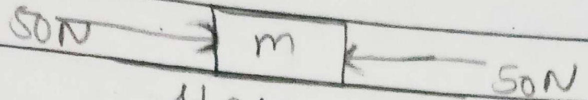
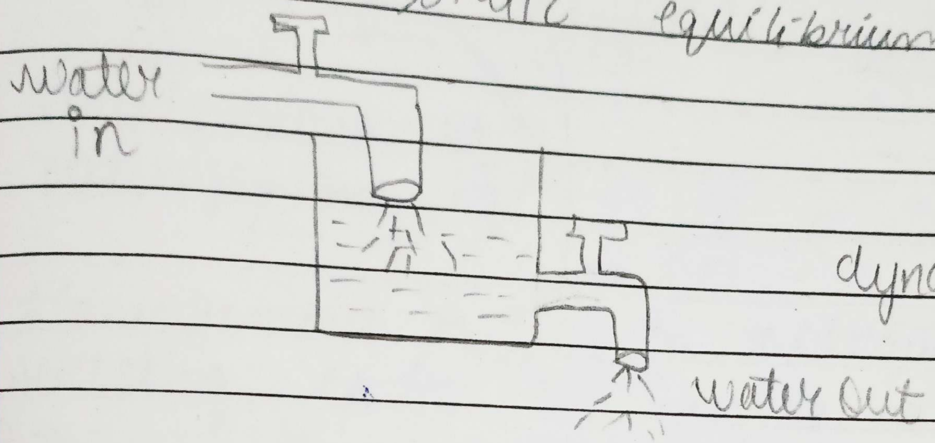
Ch-6- Equilibrium

1) "It is the process at which the conc of reactant & product does not change with time."

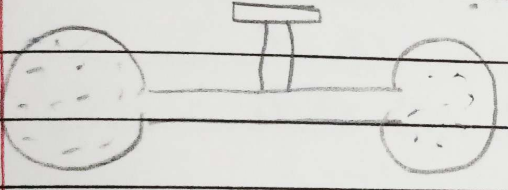
$$[R] \rightleftharpoons [P]$$

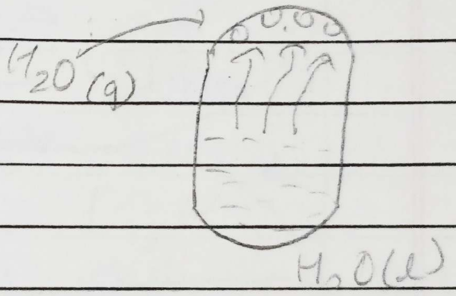


static equilibrium



dynamic equilibrium





→ [ ] → concentration → Molarity.

Equilibrium → Chemical eqn, Ionic eqn

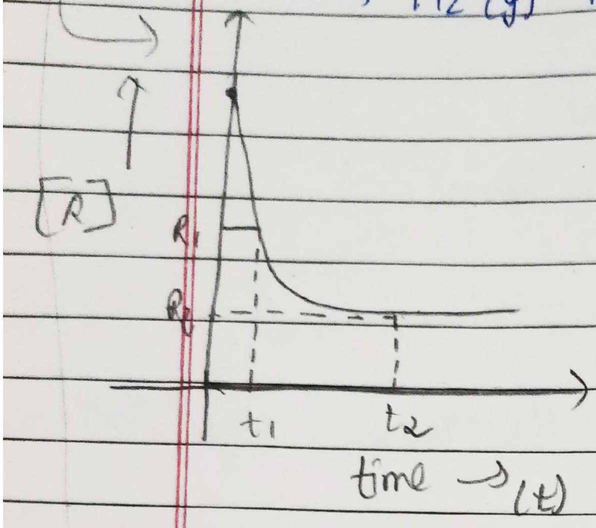
eg) (1) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

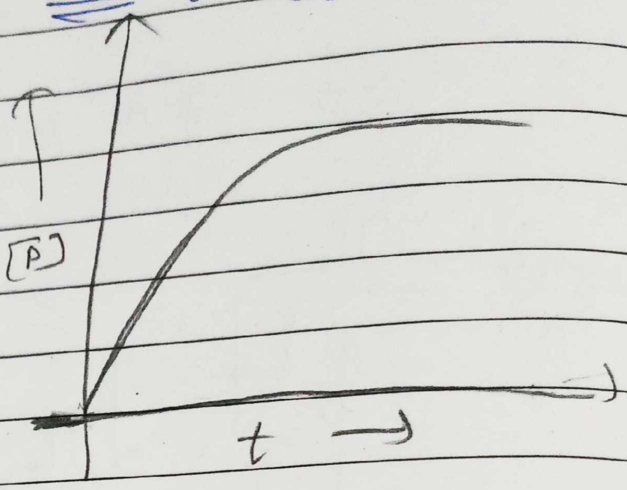
Forward rate / speed of " = Backward Rate / speed of "

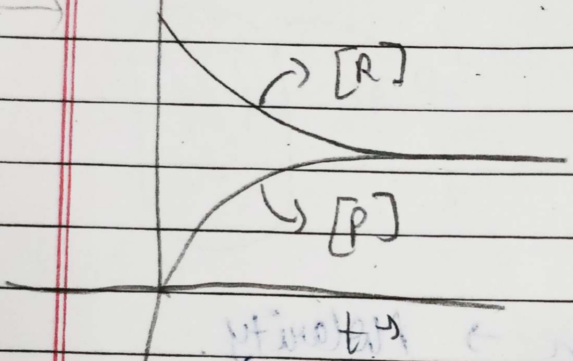
(2) $CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$

* Types of Reaction :-

1) Irreversible reaction.
2) Reversible reaction.
↳ $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$







* Characteristics of equilibrium :-

- → It is obtained in closed vessel.
- → It is obtained at constant temperature pressure & conᶜ which is the condition of reactant & product.
- → Catalyst is used to achieve early equilibrium. Once the equilibrium is established, catalyst is not used,
- → Catalyst does not change the value of ΔH° & ΔG°

$N_2(g) + 3H_2(g) \xrightarrow{Fe} 2NH_3(g)$ $\Delta H = -200 \frac{kJ}{mol}$

→ When reaⁿ is in equi., equilibrium constant is used.

$[A] \overset{K_e}{\rightleftharpoons} [B]$

→ Chemical equi. is dynamic process.

* Types of chemical equilibrium

1) Homogeneous eqᵐ
2) Heterogeneous eqᵐ

1) Homogeneous eqᵐ :- In this equi., all the reacting species are in same phase.

eg :- $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$2SO_2(g) + O_2(g) \overset{V_2O_5}{\rightleftharpoons} 2SO_3(g)$

2) Heterogeneous eqᵐ - In this equi. all the reacting species are not in same phase.

$C(s) + H_2O(l) \rightleftharpoons \underbrace{CO + H_2(g)}$ → water gas

$CaCO_3(s) \rightleftharpoons \underset{\text{quick lime}}{CaO(s)} + CO_2(g)$

* Law of Mass Action :-

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

→ Rate of forward reaction α $[A][B]$

$= k_f [A] \cdot [B]$ —— ①

→ Rate of Backward reaction $\propto [C][D]$

" $= K_b [C][D]$ — ②

from ① & ②

Forward Rate = Backward rate

$K_f [A][B] = K_b [C][D]$.

$$\frac{K_f}{K_b} = \frac{[C][D]}{[A].[B]}$$

$\frac{K_f}{K_b} = K_e$ = equilibrium constant.

$$K_e = \frac{[C][D]}{[A][B]}$$

ex :- $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

R.F.R $= K_f [N_2][H_2]$ — ①.

R.B.R. $= K_b [NH_3]$ — ②

→ at equi. condition.

$K_f [N_2][H_2] = K_b [NH_3]$

$$\frac{K_f}{K_b} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_e = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

* Types of K_e.

K_e

K_c | K_p

[ ] ⇒ con^c | K_p → gases ( )

↓ Molarity

$C = \frac{n}{V}$ | Unit ⇒ mol/litre

$PV = nRT$

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

$= CRT$

$P \propto n$

P = atm

* Value of K_p, K_c & their unit :-

Note :-

1] con^c of solid species is constant & unity = 1

2] when liquid is in equi. with gas, then con^c of liquid is unity (1)

3] When reaction is occured in aqous medium, then con^c of $[H_2O] = 1$

ex :- $Cu_{(s)} + 2Ag^+_{(aq)} \rightleftharpoons Cu^{+2}_{(aq)} + 2Ag_{(s)}$

$$K_c = \frac{[Cu^{+2}_{(aq)}][Ag_{(s)}]^2}{[Cu_{(s)}][Ag^+_{(aq)}]^2}$$

$$K_c = \frac{[Cu^{+2}]}{[Ag^+]^2}.$$

$$\text{Unit} = \frac{[mol/lit]}{[mol/lit)^2} = mol^{-1}\ lit.$$

ex :- $CH_3COOH_{(l)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}.$$

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

IMP

* Relation b/w K_p & K_c :-

→ $2A_{(g)} + 3B_{(l)} + 2C_{(s)} \rightleftharpoons D_{(g)} + E_{(g)}$

$$K_c = \frac{[D_{(g)}]\,[E_{(g)}]}{[C_{(s)}]^2\,[B_{(l)}]^3\,[A_{(g)}]^2}$$

$$K_c = \frac{[D]\,[E]}{[A]^2}$$

→ writing it according to con^c, [C] → con.

$$\boxed{K_c = \frac{[C_D]\,[C_E]}{[C_A]^2}} \text{ — ①}$$

Here,

$$K_p = \frac{(P_D)\,(P_E)}{(P_A)^2}$$

→ As per ideal gas eq^n,

$$PV = nRT$$

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

$$P = CRT$$

$$P_D = C_D RT$$

$$P_E = C_E RT$$

$$P_A = C_A RT$$

$$K_p = \frac{(C_D RT)\,(C_E RT)}{(C_A RT)^2}$$

$$= \frac{(C_D)\,(C_E)\,RT^2}{(C_A)^2\,RT^2}$$

$$K_p = \frac{K_c \cdot RT^2}{RT^2}$$

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

$$\Delta n_{(g)} = n_p - n_R$$

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

K_p = atm

K_c = mol/lit.

R = gas const.
= 0.082 lit./atm

T = Temperature

$\Delta n_{(g)} = n_p - n_R$

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1) **Case : 1** $K_p = K_c$

when $\Delta n_{(g)} = 0$. $K_p = K_c$

ex :-

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

$\Delta n_{(g)} = n_p - n_r$

$= 2 - 2$

$= 0$

2) **Case : 2** $K_p > K_c$

⇒ when $\Delta n_{(g)} > 0$.

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

$\Delta n_{(g)} = n_p - n_r$

$= 2 - 1$

$= \boxed{1}$

3) **Case : 3** $K_p < K_c$

⇒ when $\Delta n_{(g)} < 0$

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

$\Delta n_{(g)} = n_p - n_r$

$= 2 - 4$

$= \boxed{-2}$

* Characteristics of equilibrium constant :-

1) The value of equi. const. does not depends on initial conc of reactant.
2) It does not depend on catalyst.
3) It does not depend on inactive mass or inert gas.

$C + O_2 \longrightarrow CO_2$

24g 32g 44g

4) It depends on temperature.
5) It depends on type of reaction.

Ex :- $A + B \rightleftharpoons C$

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

$C \rightleftharpoons A + B$.

$K_c = \frac{[A][B]}{[C]} = \boxed{\frac{1}{K}}$.

Ex :- $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$K_c = \frac{[NO]^2}{[N_2][O_2]} = K$

$2N_2(g) + 2O_2(g) \rightleftharpoons 4NO(g)$

$K_c = \frac{[NO]^4}{[N_2]^2[O_2]^2} = \boxed{K^2}$

Ex :- $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = K$.

$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3(g)$

$K_c = \frac{[SO_3]}{[SO_2][O_2]^{1/2}} = \boxed{K^{\frac{1}{2}}}$

Ex :- $[A] \rightleftharpoons [B]$ $\qquad K_1 = \frac{[B]}{[A]}$

$+ \; [C] \rightleftharpoons [D]$ $\qquad K_2 = \frac{[D]}{[C]}$

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

$K_c = \frac{[B][D]}{[A][C]} = \boxed{K_1 \cdot K_2}$

ex:- $[A] \rightleftharpoons [B]$

$[C] \rightleftharpoons [D]$ $K_1 = [B]/[A]$

$[A]-[C] \rightleftharpoons [B]-[D]$ $K_2 = [D]/[C]$

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

$$\boxed{K_c = \frac{K_1}{K_2}}$$

ex:- $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_c = 49.$

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

$$K_c = (49)^{1/2}$$

$$\boxed{K_c = 7 = \frac{1}{7}}$$

* Significance of Keq / Prediciting the extent of reaction :-

:) $\frac{[P]_{eq}}{[R]_{eq}} = K_{eq}$

1) When, $K_{eq} > 10^3$ or $K_{eq} > 1000$

$[R] \rightleftharpoons [P]$

extent of reaction :- Highly in forward direction

2) When $K_{eq} < 10^{-3}$

$[R] \rightleftharpoons [P]$

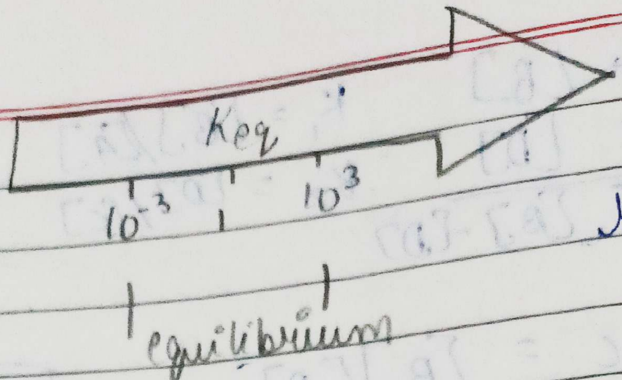
extent of reation :- Highly in backward direction.

3) when K_{eq} : $10^{-3} < K_{eq} < 10^3$

extent of reaction :- Reaction is in equilibrium

[R]

con^c is very less
reaction is not
started yet.

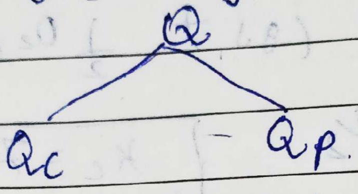


[P]

very high con^c
reaction almost
completed.

✱ Reaction Quotient :- (Q) :-

→ "Con^c of reacting species at any time t."



1) $Q_c > K_c$:- Backward side $[R \leftarrow P]$
2) $Q_c < K_c$:- Forward side $[P \rightarrow P]$
3) $Q_c = K_c$:- Reaction is in equilibrium.

✱ Degree of dissociation "α".

	A	$\rightleftharpoons$	B	$+\,C$
initial con^c	1		0	0.
at equilibrium	$1-\alpha$		α	α

Ex:-	$PCl_{5(g)}$	$\rightleftharpoons$	$PCl_{3(g)}$	$+\,Cl_{2(g)}$
initial con^c	①		0	0
at equi.	$1-0.5$		0.5	0.5.

Ex:- 5 mol of PCl_5

	$PCl_{5(g)}$	$\rightleftharpoons$	$PCl_{3(g)}$	$+\,Cl_{2(g)}$
initial	5		0	0
equi.	$5-5\alpha$		5α	5α

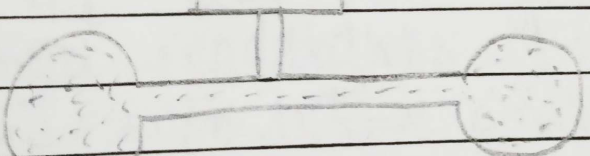
$$\alpha = \frac{\text{No. of moles dissociated}}{\text{total no. of moles of reactant.}}$$

Ex:- 1 mol of PCl_5 in 1 L vessel. so find the equi. conc of each, PCl_5, PCl_3, Cl_2 if degree of dissociation is '0.4'.

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
initial	1 mol		0		0
at equi.	$\frac{1-\alpha}{V}$		$\frac{\alpha}{V}$		$\frac{\alpha}{V}$
	$\frac{1-0.4}{1}$		$\frac{0.4}{1}$		0.4
	0.6		0.4		0.4

* Le- Chatelier's Principle :-

⇒ When equilibrium mixture is disturbed by any external force like temp., pressure, conc, it behaves like undoing the process & re- establish the equilibrium.



⇒ Temperature
⇒ pressure
⇒ conc
⇒ catalyst
⇒ Inert material

Condition.

⇒ It occurs in reversible reaction & it is in equilibrium

Forward rate = Backward rate.

$A + B \rightleftharpoons C + D.$

① concentration:-

→ When the equilibrium is disturbed by changing con^c.

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

1) If conc^n of N_2 is increased.

→ Reaction move in forward direction

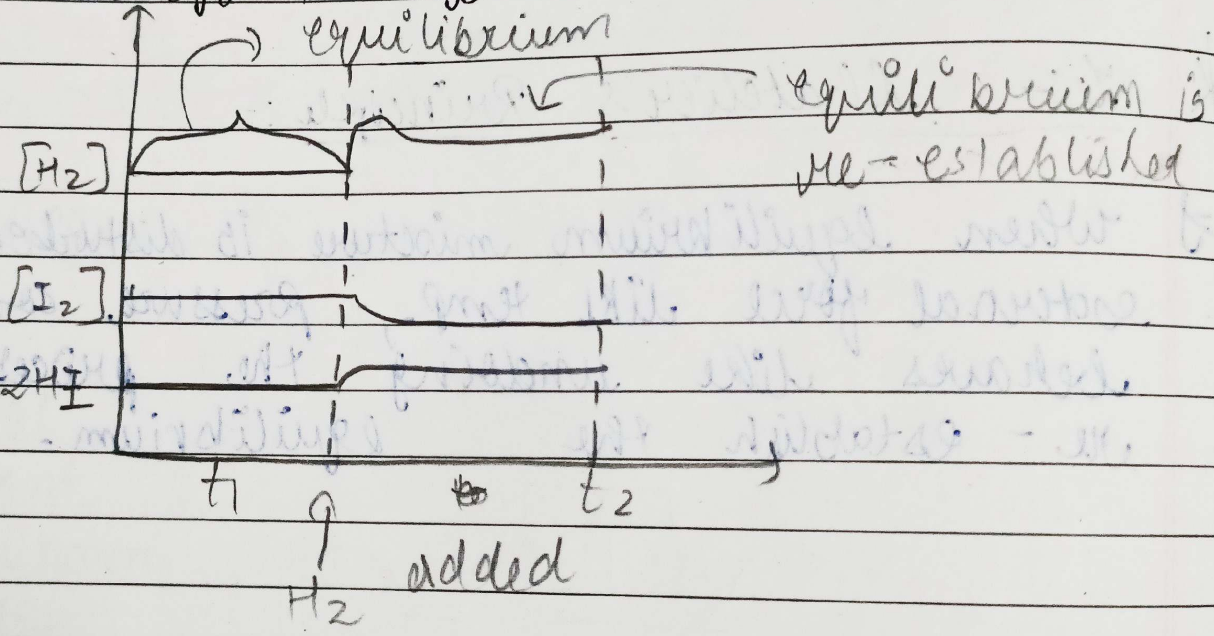
2) con^c of H_2 is 2 mol.

→ Backward direction.

3) Removal of ammonia

→ Forward direction.

eg :- $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.



Direction of reaction

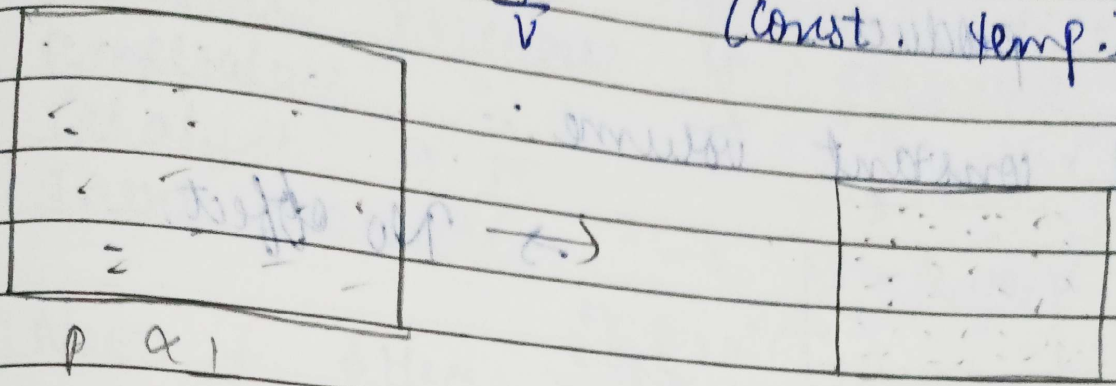
→ Higher concentration to lower con^c.

Pressure :-

→ When equilibrium is disturbed by increase pressure, reaction goes in the direction of less no. of moles is present.

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

Ex:- Boyle's Law :-
$\uparrow P \propto \frac{1}{V}$ (const. temp.)



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

concentration increases.
$C = \frac{n}{V}$ $\uparrow C \propto n \uparrow$

⇒ $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
when $\Delta n_{(g)} = 0$.
⇒ The pressure is not effected

Ex:- $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$
As pressure is decreased :- Forward direction

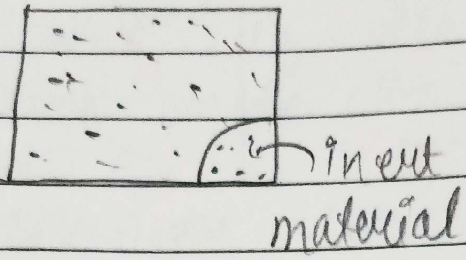
3) Temperature :-
↳ When equi. is disturbed by applying temp. the net reaⁿ goes in the direction of heat added.
⇒ $[A] + [B] + \xrightarrow{heat} C$
⇒ Forward.

⇒ Endothermic process → forward.
⇒ exothermic process → backward.

4) Inert material :-

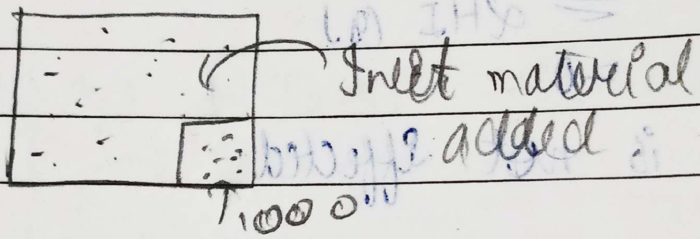
→ Inert material does not react with reactant or product.

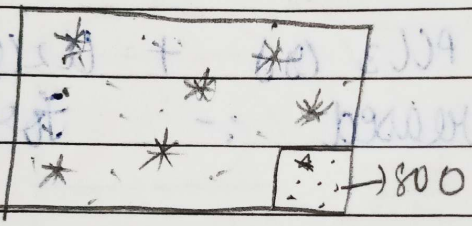
(i) at constant volume :-



→ No effect.

(i) at constant pressure :-





→ So, volume is increased.

But, the no. of molecules per unit volume is decreased.

∴ Net direction of reaction goes where the no. of moles is increased.

⑤ Catalyst :-

→ Catalyst is used to increase rate of reaction. Once the equilibrium is established, catalyst is not used.

Ex * How to increase the production of ammonia?

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

1) Con^c increase → forward direction
2) Pressure increase → forward
3) temperature " → forward
4) Catalyst → Fe → forward
5) Inert material → Backward.

$N_2(g) + 3H_2(g) \xrightleftharpoons[300\,atm]{Fe,\ 6.2KK} 2NH_3(g)$

Ex :- $H_2(g) + I_2(g) \rightleftharpoons 2HI$

$\Delta H = -230\,KJ/mol$

1) Conc^n → increase.
2) Pressure → No effect
3) Temperature → decrease

* Relation b/w Q_c, K_c, ΔG

Q_c = Reaction quotient

$Q_c < K_c$ | $Q_c > K_c$ | $Q_c = K_c$.

1) $\Delta G < 0$ → spontaneous. ∴ Forward.

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

2) $\Delta G > 0$, Non-spontaneous.

3) $\Delta G = 0$, equilibrium

$\Delta G = \Delta G^\circ + RT \ln Q_c$.

→ when reaction is in equi.

∴ $Q_c = K_c$, $\Delta G = 0$.

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

$\Delta G^\circ = -RT \ln K_c$

$\ln K_c = \frac{-\Delta G^\circ}{RT}$.

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

(i) when $\Delta G^\circ = +ve$

→ $\frac{-\Delta G^\circ}{RT} < 0$.

$e^{-\Delta G^\circ/RT} < 0$

∴ $K_c < 0$

∴ Backward.

(ii) when $\Delta G^\circ = -ve$

→ $\frac{\Delta G^\circ}{RT} > 0$.

→ $e^{-\Delta G^\circ/RT} > 0$.

→ $K_c > 0$

→ forward

* Antilog of Negative Value :-

eg :- -2.418

∴ 0.418×10^{-3}

$1 - 0.418 \times 10^{-3}$

$= 0.582 \times 10^{-3}$

$K_{c\,eq} = 3.81 \times 10^{-3}$

* Ionic equilibrium :-

$CH_3COOH \xrightleftharpoons{H_2O} CH_3COO^-(aq) + H^+(aq)$

$KOH(aq) \rightleftharpoons K^+(aq) + OH^-(aq)$

→ Michael Faraday
→ Ions are present in the solⁿ
→ But all solⁿ does not form ions.
eg:- glucose → $C_6H_{12}O_6$.

Solution

electrolyte solⁿ	non-electrolyte solⁿ
→ solⁿ which conducts electricity.	→ does not conduct electricity.
→ due to presence of ions.	→ Absence of ions.

electrolyte (solution)

weak electrolyte	strong electrolyte
→ Weak acid CH_3COOH, $HCOOH$, HCN	→ strong Acid. HCl, H_2SO_4
→ Weak Base NH_4OH	→ Strong base NaOH
→ Weak salt $(NH_4)_2CO_3$	→ Salt → NaCl

1) weak acid + weak base → weak salt.
2) strong acid + weak base → strong salt
3) weak acid + strong base → strong salt.
4) strong acid + strong base → strong salt.

eg :- $HCl + KOH \longrightarrow KCl + H_2O$
strong salt

eg :- $KCl \rightleftharpoons K^+ (aq) + Cl^- (aq)$
→ max. dissociation ($\alpha > 90\%$)

eg :- $CH_3COOH (aq) \xrightleftharpoons{5 \text{ to } 7\%} CH_3COO^-(aq) + H^+ (aq)$
Dissociation $\alpha = 5\%$

1 mol $\xrightarrow{\text{dissociate}}$ 0.05 mol

→ Range of Alpha → $\boxed{0 < \alpha < 1}$

* Arrhenius acid base Concept :-

→ Solⁿ → Aq. → H^+ ions produced → acid.

$H^+ + H_2O \rightarrow H_3O^+$
Hydronium ions.

→ Solⁿ + aq. → OH^- ions produced → base :-

eg :- $NaOH \xrightarrow{aq.} Na^+ + OH^-$
$HCl \longrightarrow H^+ + Cl^-$

* Lewis Acid - Base Concept :-

→ Acid : e^- acceptor (e^- deficient)
→ Base : e^- donor (e^- rich)

1) Acid

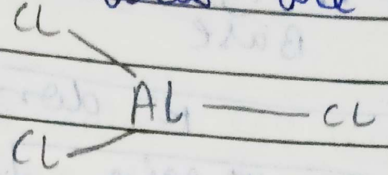
→ They are positively charged species.

ex :- Ag^+, Cu^+, H^+ or H_3O^+

→ Some neutral molecules are also lewis acid.

ex :- $AlCl_3$

BF_3



2) Lewis Base :- (nucleus loving)

→ e^- donor

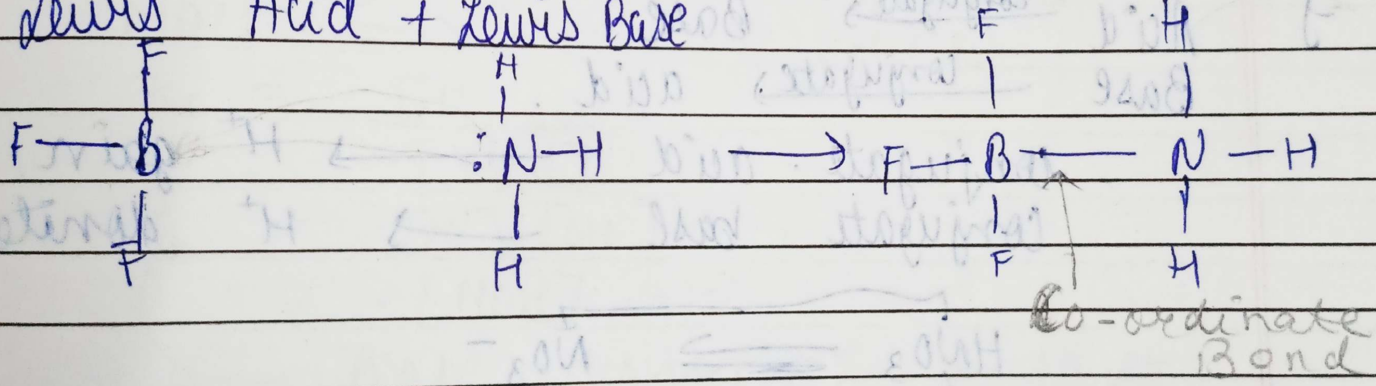
→ They are negatively charged species.

→ ex :- Cl^-, O^-, S^{-2}, F^-

→ Some neutral molecules are also lewis base.

$:NH_3$, $H_2\ddot{O}:$, $CH_3CH_2-\ddot{\underset{..}{O}}-H$

Lewis Acid + Lewis Base



* Lowry Bronsted Acid Base concept :-

→ Acid :- H^+ donate. | Base :- H^+ accept.

H^+ gain.

ex $H^+Cl^- + :H_2\ddot{O}: \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$

H^+ donate

H⁺ donate

→ $:NH_3 + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Base acid

H⁺ accept

H⁺ accept

⇒ $H^+Cl^- + :NH_3 \rightleftharpoons NH_4^+ + Cl^-$

Acid. Base

H⁺ donate

H⁺ gain.

$NH_4^+ + Cl^- \rightleftharpoons HCl + NH_3$

H⁺ donate

$HCl + NH_3 \rightleftharpoons Cl^- + NH_4^+$

Acid Base H⁺ gain. conjugate acid

conjugate base

→ Acid $\xrightarrow{\text{conjugate}}$ Base.

Base $\xrightarrow{\text{conjugate}}$ acid.

conjugate. acid → H⁺ gain.

conjugate base → H⁺ donate

$HNO_3 \rightleftharpoons NO_3^-$

Acid conjugate base.

✱ Ionisation Constant :- for Acid / Base / water.

1/ Ionisation constant for acid :-

→ Only for weak acid.

$HA \rightleftharpoons H^+(aq) + A^-(aq).$

$$K_c = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

K_a = Acid dissociation constant

or

Ionization ~~const~~ constant for acid.

→ Value of K_a depends on temp.

→ Value considered at 25°C (298 K).

→ The value of K_a does not depend on conc of reactant

→ More the $[H^+]$ conc^n → more acidic → K_a ↑

2] Ionization constant for base :-

(Only for weak base)

$$MOH \rightleftharpoons M^+_{(aq)} + OH^-_{(aq)}.$$

$$K_c = \frac{[M^+][OH^-]}{[MOH]}$$

↓

$$K_b = \frac{[M^+][OH^-]}{[MOH]}$$

→ Base dissociation constant

or

Ionization const. for base.

→ More $[OH^-]$ → more Basic → K_b ↑

extra

* Ostwald's dilution law :-

$\rightarrow \alpha$

→ The degree of dissociation of weak electrolyte is directly proportional to the square root of dilution at given temp.

$$\boxed{\alpha \propto \sqrt{V}}$$

→ $HA \rightleftharpoons H^+ + A^-$

$$Ka = \frac{[H^+][A^-]}{[HA]} \quad \text{——} ①$$

	HA	$\rightleftharpoons$ H^+	$+ A^-$
initial	1mol	0	0
at equi.	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

$$Ka = \frac{[\frac{\alpha}{V}][\frac{\alpha}{\cancel{V}}]}{\frac{1-\alpha}{\cancel{V}}}$$

$$Ka = \frac{\alpha^2}{V[1-\alpha]}$$

→ For weak solⁿ $\alpha << 5\%$.

→ Neglecting the value of α in denominator

$$\boxed{1-\alpha \approx 1}$$

$$\therefore \quad Ka = \frac{\alpha^2}{V}$$

$$\alpha = Ka \cdot \sqrt{V}$$

$$\boxed{\alpha \propto \sqrt{V}}$$

$$HA \rightleftharpoons H^+ + A^-$$

Initial $\quad C \quad\quad 0 \quad\quad 0$

at equi. $\quad \frac{C-C\alpha}{V} \quad\quad \frac{C\alpha}{V} \quad\quad \frac{C\alpha}{V}$

$$Ka = \frac{[H^+]\cdot[A^-]}{[HA]}$$

$$= \frac{\left[\frac{C\alpha}{V}\right]\left[\frac{C\alpha}{V}\right]}{\frac{C-C\alpha}{\cancel{V}}}$$

$$Ka = \frac{C^{\cancel{2}}\alpha^2}{V \times \cancel{C}(1-\alpha)} \quad [1-\alpha \simeq 1]$$

$$Ka = \frac{C\alpha^2}{V} \quad \therefore \alpha^2 = \frac{Ka\,V}{C}$$

$$\alpha = \sqrt{\frac{Ka}{C}\cdot V}$$

for 1 litre

$$\boxed{\alpha = \sqrt{\frac{Ka}{C}}}$$ → Only for weak acid

$$\boxed{\alpha = \sqrt{\frac{Kb}{C}}}$$ → Only for weak base

* Ionization constant for H_2O (Kw).

→ Self protonation / Auto protonation

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

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

$$K_c[H_2O]^2 = K_w$$

$$\boxed{K_w = [H_3O^+][OH^-]}$$ IMP

→ The value of Kw depends on temperature.

⇒ At 25°C, the value of Kw is $\boxed{K_w = 10^{-14}}$

$K_w = [H_3O^+][OH^-]$

$10^{-14} \quad x \quad x$

$x^2 = 10^{-14}$

$\boxed{x = 10^{-7}}$ ⇒ $[H_3O^+] = 10^{-7}$

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

⇒ For neutral medium

$[H_3O^+] = [OH^-]$

⇒ For acidic medium

$[H^+] > [OH^-]$

$> 10^{-7}$

⇒ For basic medium

$[H^+] < [OH^-]$

10^{-7} ex:- $10^{-8}, 10^{-9}, 10^{-10}$

⇒ $p^H + p^{OH} = 14$

$6 + p^{OH} = 14$

$\boxed{p^{OH} = 8}$

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

or

$-\log_{10}[H_3O^+]$

* Find the con^c of $[H_3O^+]$ & $[OH^-]$ ions for given weak acid HA value of Ka is 2×10^8 & the con^c of Ka is 2×10^8 & the con^c of HA is 8 mol in 2 l solⁿ.

$HA \rightleftharpoons H^+ + A^-$

initial $\quad 8 \quad 0 \quad 0$

at equill. $\quad \frac{8-8\alpha}{2} \quad \frac{8\alpha}{2}, \quad \frac{8\alpha}{2}$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{\frac{8\alpha}{2} \times \frac{8\alpha}{2}}{\frac{8-8\alpha}{2}} = \frac{8\alpha^2}{2(1-\alpha)}$$

$2 \times 10^8 = \frac{8\alpha^2}{\quad}$

$8\alpha^2 = 4 \times 10^{8}{}^{2}$

$\alpha^2 = 0.5 \times 10^8$ | $\alpha = 0.70 \times 10^4$

⇒ con^c of $[H_3O^+] = [H^+] = \frac{8\alpha}{2} = \frac{8 \times 0.70 \times 10^4}{2}$

$[H^+] = 2.8 \times 10^4$

⇒ $K_w = [H_3O^+][OH^-]$

$10^{-14} = [2.8 \times 10^4][OH^-]$

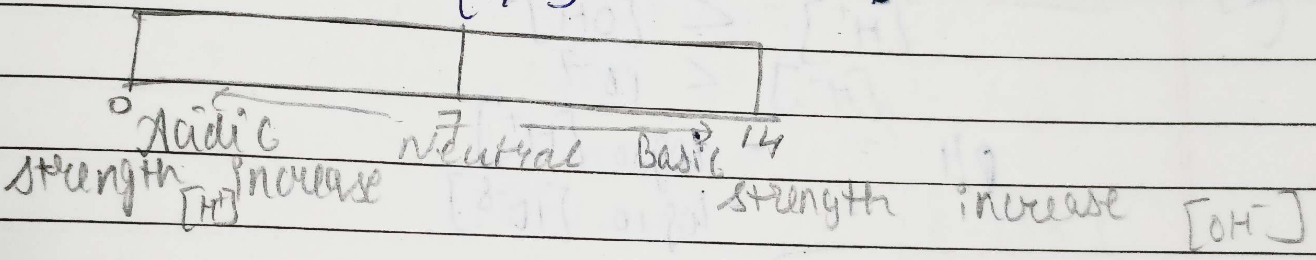
$[OH^-] = \frac{10^{-14}}{2.8 \times 10^4}$ ⇒ $[OH^-] = 0.35 \times 10^{-18}$

* pH & pOH

* pH = Potential of Hydrogen

⇒ $pH = -\log_{10}[H_3O^+]$ or $-\log[H^+]$ or

$= \log_{10}\left[\frac{1}{H^+}\right]$



⇒ W.K.T, $[H_3O^+][OH^-] = K_w$

take log on both sides,

$\log [H_3O^+][OH^-] = \log K_w$

$\log[H_3O^+] + \log[OH^-] = \log K_w$

$-\log[H_3O^+] - \log[OH^-] = -\log K_w$

$pH + pOH = pK_w$

At 25°C, $pK_w = 14$

$pH + pOH = 14$.

① For neutral medium:-

$[H_3O^+] = [OH^-]$

$K_w = \underset{x}{[H_3O^+]}\ \underset{x}{[OH^-]}$

$K_w = x^2$ | $x = 10^{-7}$

$10^{-14} = x^2$

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

$= -\log_{10} [10^{-7}]$

$= 7 \log_{10} 10$

$\boxed{pH = 7}$

2) Acidic Medium :-

$[H^+] > [OH^-]$

$> 10^{-7}$.

$p^H = -\log_{10} [H^+]$

$= -\log_{10} [10^{-6}]$ $\therefore$ $\boxed{pH = 6}$ → Acidic

3) For Basic Medium :-

$[H^+] < [OH^-]$

$[H^+] < 10^{-7}$

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

$= -\log_{10} [10^{-8}]$

$\boxed{p^H = 8}$

* Calculate the pH of 3×10^{-4} M HNO_3 Solⁿ.

$HNO_3 \longrightarrow H^+ + NO_3^-$

$3 \times 10^{-4} \longrightarrow 3 \times 10^{-4}$

$pH = -\log [3 \times 10^{-4}]$

$= -\log 3 - \log 10^{-4}$

$= -0.4771 + 4 \log 10$

$= 4 - 0.4771$

$\boxed{pH = 3.5228}$

Ex:- Calculate the pH of 10^{-8} M HCl sol^n.

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

$10^{-8}M \qquad 10^{-8}M$

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

$= -\log_{10}[10^{-8}]$ $\boxed{pH = 8}$

But, for acid pH can't be greater than 7.
which means, here, acid is more diluted.

$HCl \rightarrow [H^+] \rightarrow 10^{-8}M$

$H_2O \rightarrow [H^+] \rightarrow 10^{-7}M$

total $[H^+]$ ions $= 10^{-8} + 10^{-7}$

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

$= -\log_{10}[10^{-8} + 10^{-7}]$

$= -\log_{10}\left[10^{-8}\left(1 + \frac{10^{-7}}{10^{-8}}\right)\right]$

$= -\log_{10}[10^{-8}(1+10)]$

$= -\log_{10}[10^{-8}(11)]$

$= -[\log_{10}(10^{-8})^{a} + {}^{b}\log_{10}(11)]$

$= 8\log 10 - \log 11$

$= 8 - 1.041 = \boxed{6.958}$

* pH of Base :-

Ex:- Calculate the pH of 2×10^{-2} M sol^n of $Mg[OH]_2$

$Mg[OH]_2 \rightarrow Mg^{+2} + 2OH^-$

$2 \times 10^{-2} M \rightarrow 2 \times (2 \times 10^{-2})$

$pOH = -\log[OH^-]$

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

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

$= -0.6020 + 2$

$\boxed{pOH = 1.398}$

$pH = 14 - pOH \Rightarrow 14 - 1.398 \Rightarrow \boxed{12.602}$

* Calculate the pH of 10^{-9} M NaOH - sol^n.

$pOH = -\log[OH^-]$

$= -\log[10^{-9}]$

$pOH = 9.$

$pH = 14 - pOH$

$\boxed{pH = 5}$

But, for base pH can't be less than 7

$\therefore \Rightarrow$ $NaOH \rightarrow [OH^-] \rightarrow 10^{-9} M$

$H_2O \rightarrow [OH^-] \rightarrow 10^{-7} M.$

Total $[OH^-] = 10^{-9} + 10^{-7}$

$pOH = -\log[OH^-].$

$= -\log[10^{-9} + 10^{-7}]$

$-\log\left[10^{-9}\left(1 + \frac{10^{-7}}{10^{-9}}\right)\right].$

$= -\log[10^{-9}(1 + 100)]$

$= -\log[10^{-9}(101)]$

$= -\log 10^{-9} - \log 101$

$= 9 - 2.004$

$\boxed{pOH \Rightarrow 6.9949}$

$pH + pOH = 14$

$\therefore pH = 14 - pOH$

$= 14 - 6.9949$

$= \boxed{7.005}$

$\Rightarrow$ When given con^c is $10^{-7}, 10^{-8}, 10^{-9},$ then use water con^c.

* Normality :- (N).

(i) For Acid $\Rightarrow$ N = molarity × basicity (valency factor

(ii) For Base $\Rightarrow$ N = Molarity × Acidity eg :- $HCl \rightarrow H^+ + Cl^-$ (V.F = 1)

$H_2SO_4 \rightarrow 2H^+ + SO_4^{-2}$ (V.F = 2)

$H_3PO_4 \rightarrow 3H^+ + PO_4^{-3}$ (3)

$NaOH \rightarrow Na^+ + OH^-$ (1)

$Ca(OH)_2 \rightarrow Ca^{+2} + 2OH^-$ (2)

$(NH_4)_2CO_3 \rightarrow 2NH_4^+ + CO_3^{-2}$ (2)

eg :- pH of 0.1N HCl.

$M = \frac{N}{VF}$ ∴ $\boxed{M = 0.1}$

$pH = -\log[0.1]$

$= \boxed{0.999}$

* Calculate the pH of 2×10^{-2} N H_2SO_4 sol^n.

$M = \frac{N}{VF} = \frac{\cancel{2}\times10^{-2}}{\cancel{2}}$

$M = 10^{-2}$

$pH = -\log[10^{-2}]$

$\boxed{pH = 2}$

* pH of mixtures :-

ex :- 0.2M HCl in 2l + 0.3M HNO_3 in 1l.

Molarity = $\frac{moles}{volume}$

$0.2 = n/2$

$n = 0.2\times2$

$= 0.4$ moles

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

0.4 0.4

Molarity (M) = $\frac{moles}{volume}$

$0.3 = n/1$

moles = 0.3.

$HNO_3 \rightarrow H^+ + NO_3^-$

0.3 0.3

→ total moles of H^+ ions = 0.4+0.3 = 0.7 moles

→ total volume = 2+1 = 3l.

→ Total conc of $[H]^+ = \frac{\text{total moles}}{\text{total volume}}$

$= \frac{0.7}{3} \Rightarrow 0.233 = [H^+]$

→ $pH = -\log_{10}[H^+]$

$= -\log_{10}[0.233]$ $\boxed{pH = 0.632}$

Q.2 Find the pH of mixture:-
2×10^{-2} M NaOH solⁿ in 3 l volume +
3×10^{-3} M KOH solⁿ in 2 l volume.

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

$2\times10^{-2} = \frac{n}{3}$

$\boxed{n = 6\times10^{-2}}$

$NaOH \rightarrow Na^+ + OH^-$

6×10^{-2} 6×10^{-2}

$M = n/v$

$3\times10^{-3} = n/2$

$\boxed{n = 6\times10^{-3}}$

$KOH \rightarrow K^+ + OH^-$

6×10^{-3} 6×10^{-3}

→ total moles of OH^- $= 6\times10^{-2} + 6\times10^{-3}$
$= 6\times10^{-2} + 0.6\times10^{-2}$
$= 6.6\times10^{-2}$

total volume = 2+3 = 5 litre.

⇒ total conc of $[OH^-] = \frac{6.6\times10^{-2}}{5} = \boxed{1.32\times10^{-2}}$

$pOH = -\log[OH^-]$
$= -\log[1.32\times10^{-2}]$
$= -\log 1.32 - \log 10^{-2}$

$pOH = 0.1205 + 2 = \boxed{2.1205}$

$pH + pOH = 14$

$pH + 2.1205 = 14$

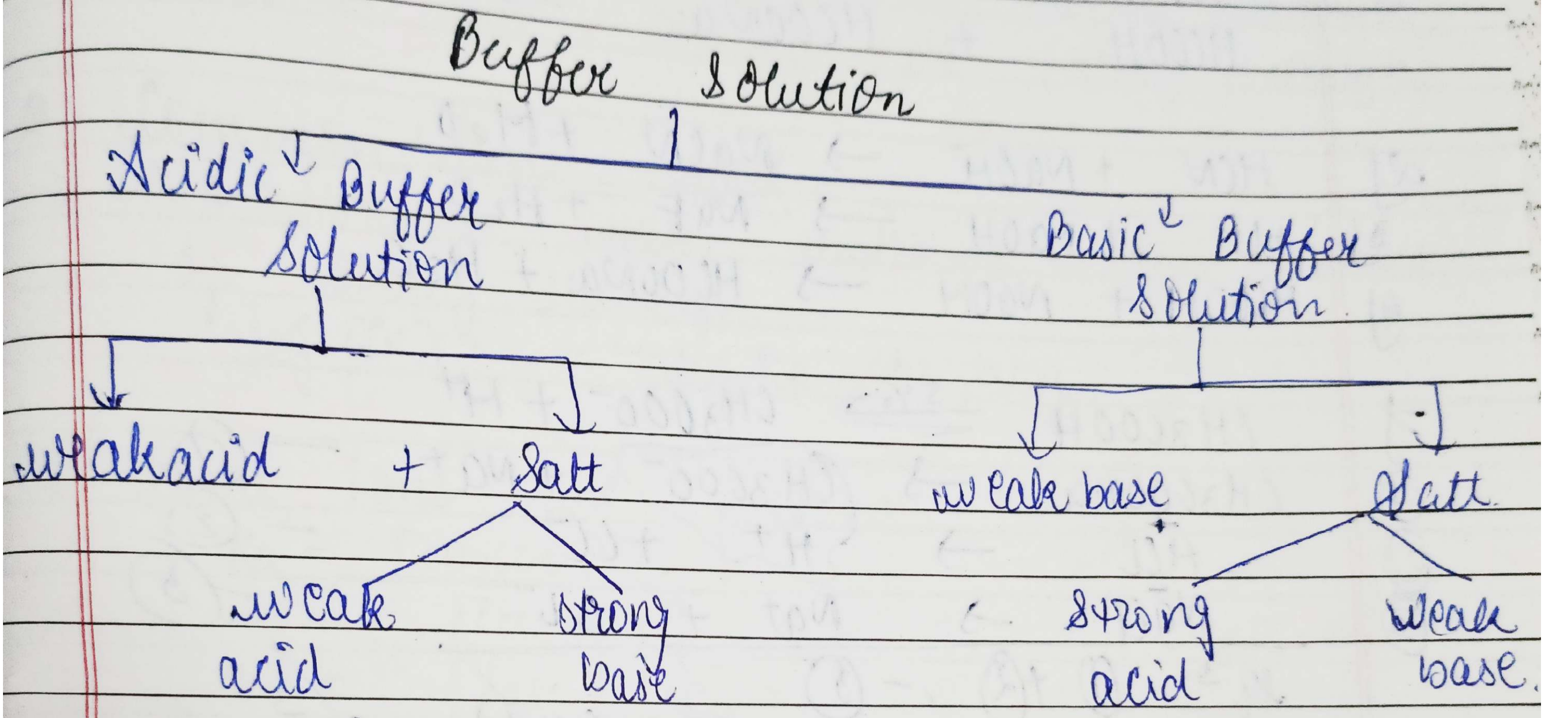
$\boxed{pH = 11.87}$

* Buffer Solution :-

→ It is the type of sol^n in which by adding Some amount of H^+ ions & OH^- ions, sol^n maintain it's pH is called buffer sol^n.

→ Its pH remains constant.

ex:- Blood → pH → 7.4.



1) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

Weak Acid — Strong Base — Salt.

2) CH_3COOH (WA) + CH_3COONa (Salt) ⟶ Acidic Buffer

3) NH_4OH (WB) + HCl (SA) $\longrightarrow NH_4Cl + H_2O$.

$NH_4OH + NH_4Cl$ ⟶ Basic Buffer sol^n.

Strong Base → group 1 & group 2 } Metal hydroxide, oxide are strong base.

NaOH, KOH, $Mg(OH)_2$, $Ca(OH)_2$

* Acidic Buffer solution:–

→ Weak Acid + Salt.

1) $CH_3COOH + CH_3COONa \rightarrow$ Acidic Buffer
$HCN + NaCN \rightarrow$ "
$HF + NaF \rightarrow$ "
$HCOOH + HCOONa \rightarrow$ "

2) $HCN + NaOH^- \rightarrow NaCN + H_2O$.
3) $HF + NaOH \rightarrow NaF + H_2O$
4) $HCOOH + NaOH \rightarrow HCOONa + H_2O$

→ $CH_3COOH \xrightleftharpoons{5\%} CH_3COO^- + H^+$
① $CH_3COONa \rightarrow CH_3COO^- + Na^+$ — ①
② $HCl \rightarrow H^+ + Cl^-$ — ②
③ $NaCl \rightarrow Na^+ + Cl^-$ — ③

eq^n ① + ② – ③
$CH_3COO^- + \cancel{Na^+} + H^+ + \cancel{Cl^-} + (\cancel{Na^+}) - \cancel{Cl^-}$
$= CH_3COO^- + H^+$ //

ex:– $H_2O \rightleftharpoons H^+ + OH^-$
$HCl \rightarrow H^+ + Cl^-$
$NaOH \rightarrow Na^+ + OH^-$
$NaCl \rightarrow Na^+ + Cl^-$

ex:– $NH_4OH \rightarrow NH_4^+ + OH^-$
$NH_4Cl \rightarrow NH_4^+ + Cl^-$
$NaOH \rightarrow Na^+ + OH^-$
$NaCl \rightarrow Na^+ + Cl^-$

* Calculate the pH of buffer solution:

* $CH_3COOH + \underbrace{CH_3COONa}_{WA + SB} \rightarrow$

Salt

⇒ $CH_3COOH \xrightleftharpoons{5\%} CH_3COO^- + H^+$ (weak electrolyte)

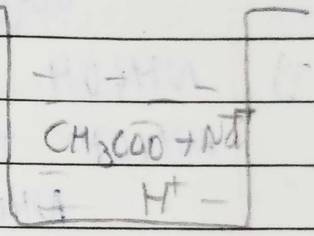
⇒ $CH_3COONa \xrightleftharpoons{95\%} CH_3COO^- + Na^+$ (strong electrolyte)

● Common ion effect:-

⇒ Dissociation of weak electrolyte in the presence of strong electrolyte.

~~log~~ $\{[H^+]\}$ = ~~log~~ Ka + ~~log~~

⇒ Same ions are present.



$$Ka = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$Ka = \frac{[Salt][H^+]}{[Acid]}$$

$$[H^+] = Ka \cdot \frac{[Acid]}{[Salt]}$$

$$\log[H^+] = \log\left[Ka \cdot \frac{[Acid]}{[Salt]}\right]$$

$$\therefore \log[H^+] = \log Ka + \log\frac{[Acid]}{[Salt]}$$

$$\Rightarrow -\log[H^+] = -\log Ka - \log\frac{[Acid]}{[Salt]}$$

$$\boxed{pH = pKa + \log\frac{[Salt]}{[Acid]}}$$

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↳ Known as Henderson Hesselbalch equation.

* Calculate the pH of buffer solution of 0.2M CH_3COOH & 0.4M CH_3COONa & value of Ka is 10^{-5}.

⇒ $pH = pKa + \log \frac{[salt]}{[Acid]}$

$pH = -\log[Ka] + \log \frac{[0.4]}{[0.2]}$

$= -\log(10^{-5}) + \log \frac{[0.4]}{[0.2]}$

$\boxed{pH = 5.3010}$

* Basic Buffer Solution :-

weak base, salt → WB + SA.

⇒ $NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$.

$NH_4OH + NH_4Cl \longrightarrow$ Basic buffer solution.

$NH_4OH \xrightleftharpoons{5\%} NH_4^+ + OH^-$

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

⇒ $K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$

$K_b = \frac{[salt][OH^-]}{Base}$

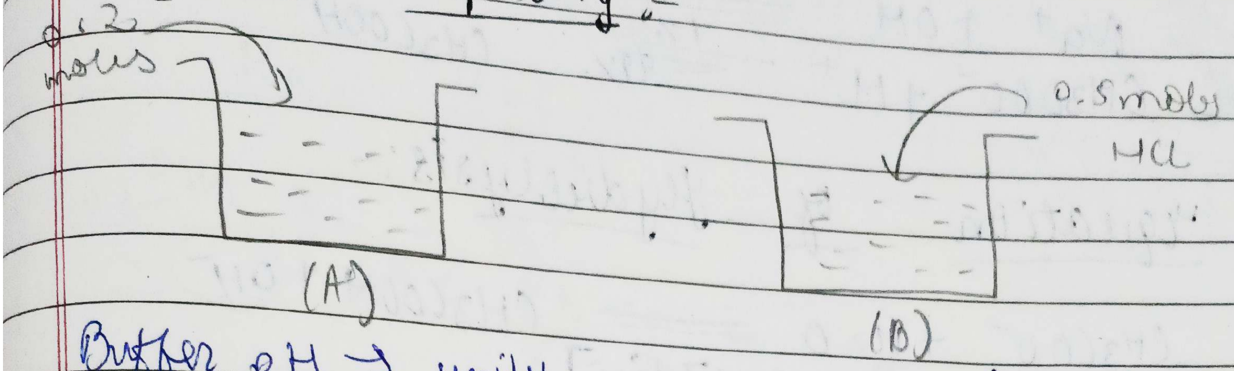
$[OH^-] = K_b \frac{[Base]}{[Salt]}$

$-\log[OH^-] = -\log K_b + \log \frac{[Salt]}{[Base]}$

$pOH = pK_b + \log \frac{[Salt]}{[Base]}$

, it some moles of H^+ or OH^- to buffer maintains its pH, but it is upto some extent, after that limit, its pH changes. ∴ that limit is known as buffer capacity.

* Buffer capacity :-



Buffer pH → unity　　pH = 1 (unity)

⇒ The no. of moles which maintains the pH of buffer solution is buffer capacity.

* Hydrolysis of Salt :-

1) Strong Acid + Strong Base = Neutral salt } N.P.
2) Weak Acid + strong Base = Basic salt
3) Strong Acid + weak Base = Acidic salt
4) weak acid + weak Base = salt.

} hydrolysis is possible

① Hydrolysis of strong Acid + Strong Base :-

$$HCl + NaOH \rightarrow NaCl + H_2O$$

$$NaCl + H_2O \rightarrow Na^+ + Cl^- + H^+ + OH^-$$

$$Na^+ + OH^- \underset{1\%}{\overset{99\%}{\rightleftharpoons}} NaOH$$

$$H^+ + Cl^- \underset{99\%}{\overset{1\%}{\rightleftharpoons}} HCl$$

⇒ ∴ Hydrolysis is not possible.

② weak acid + strong Base. → sodium acetate

$$\Rightarrow CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

$$CH_3COONa + H_2O \rightarrow CH_3COO^- + Na^+ + H^+ + OH^-$$

hydrolysis possible

$Na^+ + OH^- \xrightleftharpoons{99\%} NaOH$

$CH_3COO^- + H^+ \xrightleftharpoons[99\%]{1\%} CH_3COOH$

* equation of Hydrolysis :-

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + \boxed{OH^-}$$

sol^n → basic

$$K_c = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-][H_2O]}$$

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \quad \text{— ①}$$

$$\boxed{K_h = \text{Hydrolysis constant}}$$

* To find the value of K_h, let's find the con^c of weak acid.

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

$$\boxed{K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}} \quad \text{— ②}$$

$$K_h \times K_a = \frac{\cancel{[CH_3COOH]}[OH^-]}{\cancel{[CH_3COO^-]}} \times \frac{\cancel{[CH_3COO^-]}[H^+]}{\cancel{[CH_3COOH]}}$$

$$K_h \times K_a = [OH^-][H^+]$$

$$\boxed{\begin{gathered} K_h \times K_a = K_w \\ K_h = \frac{K_w}{K_a} \end{gathered}}$$

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO + OH^-$$

initial $\quad c \qquad 0 \qquad 0$

at equi. $\quad c-ch \qquad ch \qquad ch$

h = degree of hydrolysis.

$$K_h = \frac{[CH_3COO^-][OH^-]}{[CH_3COOH]}$$

$$K_h = \frac{[Ch][Ch]}{C(1-h)}$$

$1-\alpha \approx 1$

$\therefore 1-h \approx 1$

$$K_h = Ch^2$$

$$h^2 = \frac{K_h}{C}$$

$$\boxed{h = \sqrt{\frac{K_h}{C}}}$$

$[OH^-] = Ch$

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

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

$[H^+] = \frac{K_w}{Ch}$

$= \frac{K_w}{C\sqrt{\frac{K_h}{C}}}$

w.k.t.

$K_h = \frac{K_w}{K_a}$

$[H^+] = \frac{K_w}{C\sqrt{\frac{K_w}{K_a \times C}}}$

$[H^+] = \frac{\sqrt{K_w}\sqrt{K_w}}{\sqrt{C}\sqrt{C}\frac{\sqrt{K_w}}{\sqrt{K_a}\cdot\sqrt{C}}}$

$[H^+] = \frac{\sqrt{K_w}\cdot\sqrt{K_a}}{\sqrt{C}}$

$$\boxed{[H^+] = \sqrt{\frac{K_w \cdot K_a}{C}}}$$

* Solubility & Product of Solubility :-

⇒ Solubility (S) :- Amount of solute dissolved in 1 kg or 1 l of solⁿ.

Product of solubility

Salt

Highly soluble salt

ex :- group 1

Li^+, Na^+, K^+, Rb^+, Cs^+ or Nitrates (NO_3^-)

sparingly soluble salt or insoluble salt

→ AgCl, AgBr, $PbCl_2$, ZnS, PO_4^{-3}

* Sparingly Soluble salt :-

$$AB_{(s)} \longrightarrow AB_{(aq)} \longrightarrow A^{+}_{(aq)} + B^{-}_{(aq)}$$

Sparingly Soluble

$$AB_{(s)} \rightleftharpoons A^{+}_{(aq)} + B^{-}_{(aq)}$$

$$\frac{K}{1} = \frac{[A^{+}][B^{-}]}{[AB]}$$

K_{sp} = sparingly soluble salt constant

$$K_{sp} = [A^{+}][B^{-}]$$

→ saturated solution

→ The value of K_{sp} depends on temp.

* Product of Solubility :-

① Type :- A:B or 1:1

ex:- $AgCl \longrightarrow Ag^{+} + Cl^{-}$

$AgBr \longrightarrow Ag^{+} + Br^{-}$

$PbSO_4 \longrightarrow Pb^{+2} + SO_4^{-2}$

ex:- $AB_{(s)} \longrightarrow A^{+} + B^{-}$

1 (S) (S)

$$K_{sp} = \frac{[A^{+}][B^{-}]}{[AB]}$$

$$K_{sp} = [S][S]$$

$$K_{sp} = S^{2}$$

② Type :- $A_2B \rightarrow 2:1$

or

$AB_2 \rightarrow 1:2$

ex :- $PbCl_2$

$$PbCl_2 \longrightarrow \underset{S}{Pb^{+2}} + \underset{2S}{2Cl^-}$$

$$Ksp = \frac{[Pb^{+2}][Cl^-]^2}{[PbCl_2]}$$

$$Ksp = [S][2S]^2$$

$$\boxed{Ksp = 4S^3}$$

③ Type :- $AB_3 \rightarrow 1:3$ or

$A_3B \rightarrow 3:1$

ex:- $$\underset{1}{AlCl_3(s)} \longrightarrow \underset{(s)}{Al^{+3}} + \underset{(s)}{3Cl^-}$$

$$Ksp = \frac{[Al^{+3}][Cl^-]^3}{[AlCl_3]}$$

$$Ksp = [S][3S]^3$$

$$\boxed{Ksp = 27S^4}$$

④ Type :- $A_2B_3 \rightarrow 2:3$ or

$A_3B_2 \rightarrow 3:2$

ex :- As_2S_3

$$A_2B_3(s) \longrightarrow \underset{2S}{2A^+} + \underset{3S}{3B^-}$$

$$Ksp = [A]^2[B]^3$$

$$= [2S]^2[3S]^3 = \boxed{108S^5}$$

cube root $= 2\sqrt{} \times 4\sqrt{} \times 8 \times \sqrt{} \times 2\sqrt{} =$

ex :- Find the solubility of $PbCl_2$ at 25°C when $K_{sp} = 1 \times 10^{-15}$

$$PbCl_2 \longrightarrow \underset{s}{Pb^{+2}} + \underset{2s}{2Cl^-}$$

$$K_{sp} = [Pb^{+2}][Cl^-]^2$$
$$1 \times 10^{-15} = [s][2s]^2$$
$$1 \times 10^{-15} = 4s^3$$
$$s^3 = \frac{1 \times 10^{-15}}{4}$$
$$s^3 = 0.25 \times 10^{-15}$$
$$s = \sqrt[3]{0.25 \times 10^{-15}}$$
$$\boxed{s = 0.6299 \times 10^{-5}}$$

ex 6.26
M. IMP

$$K_{sp} = 1.1 \times 10^{-23}$$
$$A_2X_{3}(s) \longleftrightarrow \underset{2s}{2A^+} + \underset{3s}{3X^-}$$
$$K_{sp} = [A^+]^2[X^-]^3$$
$$1.1 \times 10^{-23} = [2s]^2 [3s]^3$$
$$1.1 \times 10^{-23} = 108 s^5$$
$$s^5 = \frac{1.1 \times 10^{-23}}{108}$$
$$s^5 = 0.010 \times 10^{-23}$$
$$s^5 = 1.0 \times 10^{-25}$$
$$= 1 \times 10^{-25\,(1/5)}$$
$$\boxed{s = 1 \times 10^{-5}}$$