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ionic equilibrium

arrhenius
lewis
bronstede lowry.

Electrolytes:

- on the basis of their dissociation nature:

(A.) Strong electrolytes:
→ substances which are largely dissociated and are strong electrolytes.
eg: HCl, HNO_3, H_2SO_4, etc.

(B.) Weak electrolytes:
→ substances which dissociate only to a small extent in aqueous solution.
eg: HCN, H_3BO_3, etc.

(C.) Non electrolytes:
→ which do not dissociate.
maltose H_{21}
eg: Glucose, Urea (NH_2CONH_2), sucrose [$C_{12}H_{22}O_{11}$], etc.

Acid-Base Concept:

(A.) Arrhenius concept: (1880-1890)
→ according to him,
- substances which releases H^+ or H_3O^+ ion in aqueous solution are ACID.
- substances which releases OH^- ion in aqueous solution are BASE.

eg: **ACID**: HCl, HNO_3, H_2SO_4, etc.
BASE: $Mg(OH)_2$, $Ca(OH)_2$, $NaOH$, etc.

* Limitations:

- it didn't justify acidic nature of $AlCl_3$, BF_3, PCl_3, and basic nature of $\ddot{N}H_3$ (ammonia), ether (COR), $CH_3-\ddot{O}CH_3$, $C_2H_5\ddot{O}H$, etc.

(B.) Lewis concept: (1923)

→ according to him,

- substances which accept lone paired electrons are known as **LEWIS ACID**.

- substances which donate lone paired electrons are **LEWIS BASE**.

$$\overset{\curvearrowleft}{A + \ddot{B}}$$

(lewis acid) (Lewis base)

(l.p acceptor) (l.p donator).

eg: **L.ACID**: $AlCl_3$, BF_3, PCl_3, $FeCl_3$, Cu^{+2}, Fe^{+2}, etc.
L.BASE: $\ddot{N}H_3$, $C_2H_5\ddot{O}H$, $CH_3-\ddot{O}-CH_3$, ligands, etc.

> * $AlCl_3$, BF_3 : octate deficient
> PCl_3, $FeCl_3$: vacant d-orbital
> $R\ddot{N}H_2$: amines (l.base).
> Ligands: (CO, CN^-, H_2O, NH_3, etc.)

(c.) <u>Bronsted lowry concept:</u> (1923)

→ according to him,

- substances who donate protons (H^+) are <u>ACIDS</u>.

- substances who accepts protons (H^+) are <u>BASE</u>.

$$\underset{\text{acid-1}}{HCl} + \underset{\text{base-1}}{NH_3} \rightleftharpoons \underset{\text{base-2}}{Cl^-} + \underset{\text{acid-2}}{NH_4^+}$$

* Water is amphoteric in nature. As It shows acidic behaviour with base and basic behaviour with acids.

$$\underset{\text{acid-1}}{HCl} + \underset{\text{base-1}}{H_2O} \rightleftharpoons \underset{\text{base-2}}{Cl^-} + \underset{\text{acid-2}}{H_3O^+}$$

$$\underset{\text{base-1}}{NH_3} + \underset{\text{acid-1}}{H_2O} \rightleftharpoons \underset{\text{acid-2}}{NH_4^+} + \underset{\text{base-2}}{OH^-}$$

- pair of acid and base should be obtained which can be known as <u>Conjugated acid-base-pair</u>.

- Conjugated acid-base pair differs by only 1 proton (H^+).

- a strong acid have weak conjugated base and a strong base have weak conjugated acid.

Q:1 Find conjugated acid and base of:

→

(A)	$HCO_3^- \longrightarrow$	H_2CO_3	CO_3^{2-}
(B)	$CO_3^{2-} \longrightarrow$	HCO_3^-	~~CO_3^{3-}~~ not possible.
(C)	$HPO_4^{2-} \longrightarrow$	$H_2PO_4^-$	PO_4^{3-}
(D)	$Cl^- \longrightarrow$	HCl	–
		conjugated acid	conjugated base

* here, HCO_3^-, HPO_4^{2-} are amphoteric.

Q:2 Conjugate base of Bronsted acid H_2O and HF are:

OH^- H^+ H^+ F^-

→ OH^- and F^-

Kw # Ionic product of water and Ionisation constant for water:

- water is a weak electrolyte because only one molecule electrolyse of 10,000 molecules.

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

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

$$K[H_2O] = [H^+]\cdot[OH^-]$$

$$Kw = [H^+]\ [OH^-]$$

- at 25°C, value of Kw is 10^{-14}.

$$Kw = [H^+][OH^-] = 10^{-14} \quad @\ 25°C.$$

$$[H^+] = [OH^-] = 10^{-7} \text{ (neutral state)}$$

→ if $[H^+] > 10^{-7} \longrightarrow$ acidic

if $[OH^-] > 10^{-7} \longrightarrow$ basic

→ if $[H^+] < 10^{-7} \longrightarrow$ basic

if $[OH^-] < 10^{-7} \longrightarrow$ acidic.

→ if $[H^+] > [OH^-] \longrightarrow$ acidic

if $[OH^-] > [H^+] \longrightarrow$ basic.

- at 90°C temp value of $K_w = \underline{10^{-12}}$

$K_w = [H^+][OH^-] = 10^{-12}$ @ 90°C

$[H^+] = [OH^-] = 10^{-6}$

K_w = equilibrium constant of water.
= dissociation constant of water.
= ionisation constant of water.

Ostwald dilution law:

- Ostwald was the first scientist to apply law of mass action to ionic equilibrium.

- it is applicable only for weak electrolytes.

- according to this law,
  → when solution of weak electrolyte is diluted then degree of ionisation (α) of solution is increased.

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

	$AB_{(aq)}$	$A^+_{(aq)}$	$B^-_{(aq)}$
initial:	C	0	0
concⁿ at eq:	$C-x$	x	x
	$C-C\alpha$	$C\alpha$	$C\alpha$

$\alpha = \frac{x}{C}$

$x = C\alpha$.

$$K = \frac{[A^+][B^-]}{[AB]} \longrightarrow \frac{C^{\cancel{2}}\alpha^2}{\cancel{C}(1-\alpha)} \qquad \boxed{K = \frac{C\alpha^2}{(1-\alpha)}}$$

here, $\alpha <<<< 1$. $(K = C\alpha^2)$

$$\boxed{\alpha = \sqrt{\frac{K}{C}}} \qquad \boxed{C \propto \frac{1}{V}} \qquad \boxed{\begin{array}{l}\alpha\,(DOD) \propto \sqrt{V} \\ \alpha\,(DOD) \propto \sqrt{\text{dilution}}\end{array}}$$

- for, weak electrolytes 'α' is directly proportional to square root of dilution or inversely proportional to square root of concentration.

$\alpha \propto \sqrt{\text{dilution}}$ $\qquad$ $\alpha \propto \sqrt{\frac{1}{\text{concentration}}}$.

$*$ NOTE:
→ at ∞ dilution value of α equals to 1. (100%)

Application of Ostwald dilution:

1.) To determine ionisation constant of weak acid (Ka):

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

initial conc^n: C 0 0

conc^n at eq: $C - C\alpha$ $c(1-\alpha)$ $C\alpha$ $C\alpha$

$K_a = \frac{[H^+][A^-]}{[HA]} \longrightarrow K_a = \frac{c^{\cancel{2}}\alpha^2}{\cancel{c}(1-\alpha)}$ $(\alpha <<< 1)$

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

$\longrightarrow H^+ = C\alpha$ $\left(\because \alpha = \sqrt{\frac{K_a}{C}}\right)$

$\therefore$, $\boxed{H^+ = \sqrt{K_a \times C}}$

II.) Determine pH of weak base:

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

initial conc^n: C 0 0

conc^n at eq: $C(1-\alpha)$ $C\alpha$ $C\alpha$.

$K_b = \frac{[B^+][OH^-]}{[BOH]} \longrightarrow K_b = \frac{C^{\cancel{2}}\alpha^2}{\cancel{C}(1-\alpha)}$ $(\alpha <<< 1)$

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

$\longrightarrow OH^- = C\alpha$ $\left(\because \alpha = \sqrt{\frac{K_b}{C}}\right)$.

$\therefore$, $\boxed{OH^- = \sqrt{K_b \times C}}$