

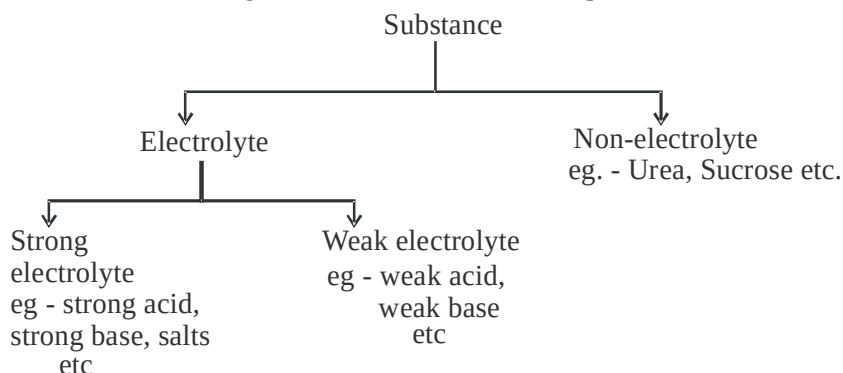


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IONIC EQUILIBRIUM

The study of reactions involving ions is studied under ionic equilibrium.



DISSOCIATION OF WEAK ELECTROLYTES

Weak electrolytes are not completely ionized when dissolved in polar solvents. The equilibrium is set up between ionized and unionized molecule in solution.

Degree of Dissociation

The degree of dissociation (α) of weak electrolytes is much less than unity.

$$\alpha = \frac{\text{No. of molecules dissociated as ions}}{\text{Total number of molecules of electrolytes dissolved}}$$

ACID AND BASE DISSOCIATION CONSTANT

Let us consider the dissociation of a weak acid,

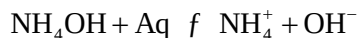


$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{H}_3\text{C}-\text{COOH}]}, \text{ Here } K_a \text{ is acid dissociation constant.}$$

Larger is the $[\text{H}_3\text{O}^+]$ concentration, larger will be the K_a value and thus larger is the strength of acid.

BASE DISSOCIATION CONSTANT (K_b) :

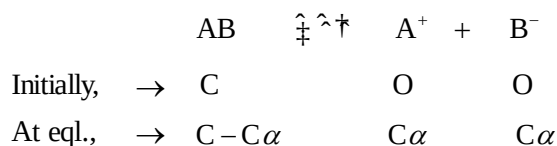
Let us consider the dissociation of weak base.



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

OSTWALD DILUTION LAW :

Let us consider the dissociation of weak electrolyte AB.



$$\therefore k = \frac{\text{C}\alpha^2}{\text{C}(1-\alpha)}$$

For very weak electrolytes

$$\alpha \ll 1$$

$$\therefore \alpha = \sqrt{\frac{k}{c}} \quad \text{where } k = \text{dissociation constant.}$$

The degree of dissociation of weak electrolyte is proportional to square root of dilution.

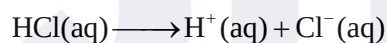
$$\alpha = \sqrt{\frac{K_a}{c}}, \quad \alpha = \sqrt{\frac{K_b}{c}}$$

where, K_a = Acid dissociation constant

and K_b = Base dissociation constant

CONCEPT OF ACID AND BASEI. ARRHENIUS CONCEPT :

Acid : A substance which ionises in water to produce H^+ ion is acid.



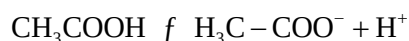
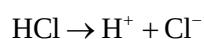
Base : A substance which produces $\text{OH}^-(\text{aq})$ in water is called base.



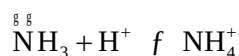
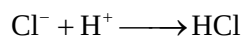
But the Arrhenius concept is limited to aqueous solutions and there are few other limitation in this theory.

II. THE BRONSTED-LOWRY'S CONCEPT

Acid : Proton (H^+) donor is acid



Base : Proton acceptor is base

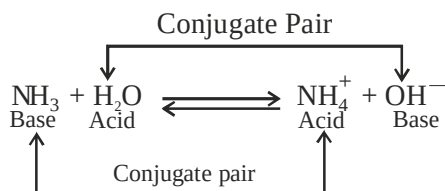


Thus Cl^- and NH_3 are Bronsted base.

Conjugate acid-base pair

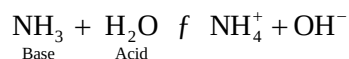
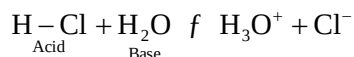
The acid base pair which differs by a proton (H^+) is called conjugate pair.

The conjugate pair of acid is always a base and that of a base it is always a acid.

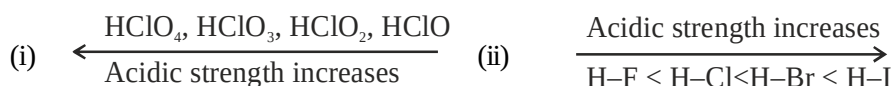


Amphoteric behaviour

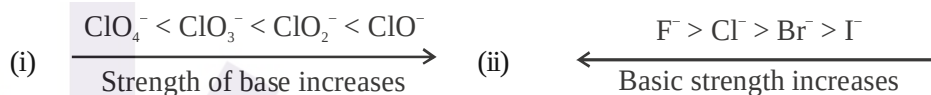
Substance which can act as acid and base in different reaction is called amphoteric substance



Strength of Bronsted Acid and Base



The conjugate pair of strong acid is weak base and vice-versa.



Hydrated protons and hydronium ions :

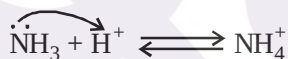
H^+ gets bonded to oxygen of H_2O to exist as H_3O^+ in aqueous solution. H_3O^+ is trigonal pyramidal.

Other hydrated species are H_5O_2^+ , H_7O_3^+ , H_9O_4^+ .

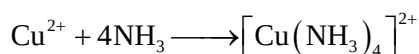
III. LEWIS ACID-BASE CONCEPT

Acid : Electron pair acceptor are Lewis acid

Base : Electron-pair donor is Lewis base



Since, NH_3 donates a electron pair, it is base.

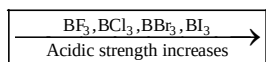


Here, Cu^{2+} accepts electron pair from NH_3 thus Cu^{2+} is acid.

Some Common Lewis Acids :

- (a) Molecules in which central atom has incomplete octet due to the deficiency of at least a pair of electron are Lewis acid.

Examples - BF_3 , BCl_3 , AlCl_3 , MgCl_2 , BeCl_2 etc.



This can be explained by back-bonding concept.

- (b) Simple Cations : H^+ , Ag^+ , Cu^+ etc.

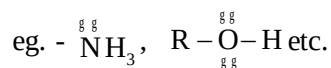
- (c) Molecules in which central atom has vacant d orbital : SiCl_4 , GeCl_4 , TiCl_4 , SnCl_4 , PCl_3 , PCl_5 , SF_4 etc

- (d) Molecules having a multiple bond between atom of dissimilar electronegativity.

eg. - CO_2 , SO_3 , SO_2

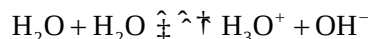
Some Examples of Lewis base

(a) Neutral species having at least one lone pair of electron to donate are Lewis base.



(b) Negatively charged species : Cl^- , Br^- , NH_2^-

Ionic Product of water (K_w) : Let us consider the self dissociation of H_2O .



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

The value of K_w increases with increase in temperature and at 25°C , K_w is 1×10^{-14} . since pure water is neutral, thus $[\text{H}_3\text{O}^+] = [\text{OH}^-]$

$$\therefore [\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ moles litre}^{-1}$$

HYDROGEN ION CONCENTRATION AND pH SCALE :

This concept was given by Sorenson in 1909.

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

Thus pH is defined as the negative logarithm concentration (in moles per litre) of hydrogen ion.

Similarly, $\text{pOH} = -\log [\text{OH}^-]$

RELATION BETWEEN pH AND pOH :

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 1 \times 10^{-14}$$

Taking negative log on both sides

$$\text{pH} + \text{pOH} = \text{p}K_w = 14$$

where $\text{p}K_w = -\log K_w$

pH Scale :

$[\text{H}^+]$	$[\text{OH}^-]$	pH	pOH	Nature of Solution
10^0	10^{-14}	0	14	Strongly acidic
10^{-2}	10^{-12}	2	12	Acidic
10^{-5}	10^{-9}	5	9	Weakly acidic
10^{-7}	10^{-7}	7	7	Neutral
10^{-9}	10^{-5}	9	5	Weakly basic
10^{-11}	10^{-3}	11	3	Basic
10^{-14}	100	14	0	Strongly basic

BUFFER SOLUTION

A solution whose pH is not affected to great extent by the addition of few drop of either acid or base is called buffer solution.

- (i) Acidic Buffer : $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ - Weak acid its salts of any strong bases.
 (ii) Alkaline Buffer: $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ - Weak acid and its salts of any strong acid.

HENDERSON EQUATION (pH OF A BUFFER):

$$\text{For acidic buffer} = \text{pH} = -\log K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

$$\text{or, } \boxed{\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}}$$

$$\text{For Alkaline buffer : } \boxed{\text{pOH} = \text{pK}_b + \log \frac{[\text{salt}]}{[\text{Base}]}}$$

Buffer Capacity : The property of a buffer solution to resist any change in its pH value is called buffer capacity.

$$\text{Buffer Capacity} = \frac{\text{No. of moles of Acid or Base added to 1 litre}}{\text{Change in pH}}$$

HYDROLYSIS OF SALT

The reaction of salt with water is called its hydrolysis.

1. Hydrolysis of salt of Weak Acid with a strong Base

Examples : CH_3COONa , Na_2CO_3 , KCN , Na_3PO_4 , Na_2S , Borax etc.

If K_h = hydrolysis constant of salt

$$\therefore K_h = \frac{K_w}{K_a} \quad \dots(i)$$

and degree of hydrolysis of salt is h

$$h = \sqrt{\frac{K_h}{C}} \quad \dots(ii)$$

where C = initial molar concentration of salt

Comparing Equation (i) and (ii)

$$\boxed{h = \sqrt{\frac{K_w}{K_a \cdot C}}}$$

$$\boxed{\text{pH} = 7 + \frac{1}{2} \text{pK}_a + \frac{1}{2} \log C}$$

2. Hydrolysis of salt of strong acid and a weak base:

Examples : $(\text{NH}_4)_2\text{SO}_4$, CaNO_3 , FeCl_3 etc.

$$k_h = \frac{k_w}{k_b} \quad \text{and } Q h = \sqrt{\frac{K_h}{C}}$$

$$\therefore h = \sqrt{\frac{K_w}{K_b \cdot C}} \quad \text{and} \quad \boxed{\text{pH} = 7 - \frac{1}{2} \text{pK}_b - \frac{1}{2} \log C}$$

3. Hydrolysis of salt of weak acid and a weak base

Examples : $\text{CH}_3\text{COONH}_4$, BaCO_3

$$K_h = \frac{K_w}{K_a \times K_b} \quad \text{and} \quad h = \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_a - \text{p}K_b)$$

4. Hydrolysis of salt of strong acid and strong base

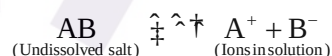
Example NaCl



Thus, salt do not undergo hydrolysis.

SOLUBILITY PRODUCT

If a sparingly soluble salt (like AgCl , BaSO_4 etc) is put in water, very little amount of it dissolves in water and the solution becomes saturated. Equilibrium is established between the undissolved salt and the ions in solution.



Applying the law of mass action, we get

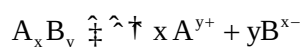
$$K = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]} \quad \text{or} \quad K[\text{AB}] = [\text{A}^+][\text{B}^-]$$

But since only a little of the salt AB goes into solution, the concentration of undissolved salt nearly remains constant.

Hence, $K \times \text{constant} = K_{sp}$

Where K_{sp} is another constant and is known as solubility product of the salt AB .

For general study let us discuss the sparingly soluble compound A_xB_y .



Hence the solubility product of such salt, $K_{sp} = [\text{A}^{y+}]^x \times [\text{B}^{x-}]^y$

From the above expression of solubility product, it is obvious that

- When the ionic product is equal to solubility product, the solution is just saturated, and no precipitation occurs.
- When the ionic product is less than the solubility product, the solution is unsaturated and more of the salt can be dissolved in it, and thus no precipitation is observed.
- When the ionic product exceeds the solubility product, the solution is super-saturated, and precipitation will occur.

Remember that solubility product of an electrolyte is a constant value at a particular temperature and it is the largest limit of ionic product of the electrolyte in solution.

RELATION BETWEEN SOLUBILITY PRODUCT AND SOLUBILITY

(i) For AB type : $AB \rightleftharpoons A^+_s + B^-_s$

$$\therefore S = \sqrt{K_{sp}}$$

(ii) For ternary type (AB_2) : say Ag_2CrO_4 , PbI_2 , etc

$$K_{sp} = (2S)^2 \times S = 4S^3$$

$$S^3 = \frac{K_{sp}}{4}$$

$$S = \left[\frac{K_{sp}}{4} \right]^{1/3}$$

(iii) For AB_3 type: e.g. $Al(OH)_3$

$$K_{sp} = [Al^{3+}][OH^-]^3 = 27S^4$$

$$\Rightarrow S = \left(\frac{K_{sp}}{27} \right)^{1/4}$$

(iv) For A_3B_2 type: e.g. $Ca_3(PO_4)_2$

$$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2 = 108 S^5$$

$$S = \sqrt[5]{\frac{K_{sp}}{108}}$$