

Ionic Equilibrium

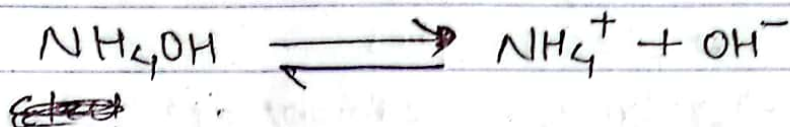
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The process of breaking a chemical compound into its ions is called ionization.

The state of dynamic equilibrium between the ions of an electrolyte and its unionized molecules in ~~solution~~ in aqueous solution is called ionic equilibrium.

e.g.



Forward reaction is called ionization/dissociation reaction and the backward reaction is called association reaction.

* Electrolytes:

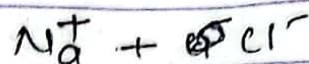
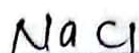
The substance which conduct electricity in molten or in solution state and get decomposed during the passage of current are called electrolytes.

Types: → (2 types)

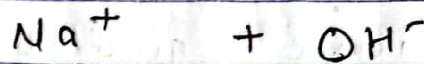
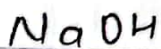
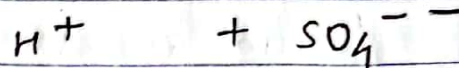
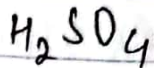
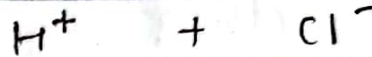
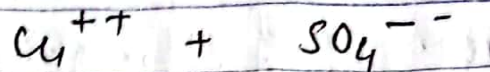
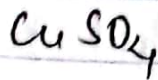
② Strong electrolytes:

The electrolytes which are almost completely ionize (dissociate into ions) when dissolve in water are called strong electrolytes.

Examples,



ions in solution.

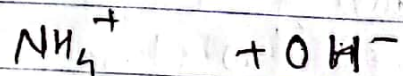
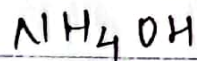
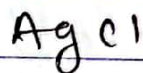
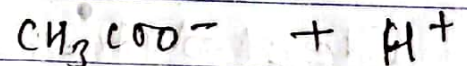
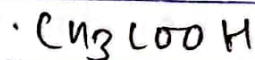


Strong electrolyte conduct electricity in solution. State

⑤ Weak electrolytes.

The electrolyte which are ionized to a very small extent (feebly ionized) in solution are called weak electrolytes.

They do not conduct electricity
e.g.



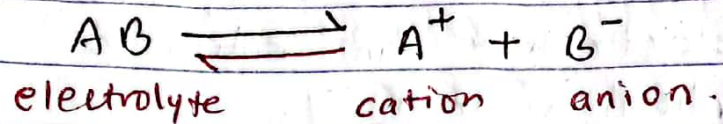
Arrhenius Theory of Ionization.

The successful theory of ~~electrolytic~~ ionization of electrolyte in solution was given by S. Arrhenius in 1887.

The main postulates of Arrhenius theory of ionization are as follows.

1. When an electrolyte is dissolved in water it dissociates into oppositely charged particles called ions. This process is called ionization.
 - Positively ~~charged~~ charged ions are cations.
 - Negatively charged ions are anions.
2. In an electrolytic solution, the total no of positive charge (cations) is equal to negative charge (anions) so that the solution is electrically neutral.
3. When the electricity is passed through the ~~solution~~, electrolytic solution, cation moves towards cathode while anions move towards anode.
4. There is a state of equilibrium between the ionized (ions) and unionized molecules of electrolyte. Such equilibrium is characterized by an ~~ionization~~ constant called —

- Ionization constant or dissociation constant
i.e. ~~is~~ If an electrolyte AB ionizes then,



So, ionization constant K_{eq} is given by

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

6. Q.

5. Ionization is an incomplete process. The extent of ionization of an electrolyte is expressed in terms of degree ionization (α). It is the fraction of total no. of moles present ~~is~~ ~~as~~ as free ions in the solution.

$$\alpha = \frac{\text{Number of molecule ionized}}{\text{Total no of molecule dissolved}}$$

For strong electrolyte α is nearly 1.

For weak electrolyte α is less than 1.

6. The electrical conductivity is due to migration of ions towards oppositely charged electrodes.
7. The properties of electrolytes in solution are the properties of ions.

Limitation of Arrhenius theory of ionization:-

1. This theory is only applicable for weak electrolyte. It cannot be applicable for strong electrolyte, as there does not exist dynamic equilibrium.
2. This theory is limited to the ionization of electrolyte in water only but ionization can occur in a molten state or absence of water also.

Ionization of weak Electrolytes: Ostwald's dilution law.

Ostwald's dilution law describes the dependence of ionization of weak electrolytes with concentration and gives the mathematical relationship between degree of ionization ~~and~~ dilution.

It states that "At constant temperature an electrolyte gets ionized to a large extent with increasing dilution."

Let n moles of an electrolyte ~~are~~ are dissolved in ' V ' litres of solution. Then degree of ionization of the electrolyte will

be

$$\alpha = \frac{\text{no. of molecules splitted into ions.}}{\text{Total no. of molecules dissolved.}}$$

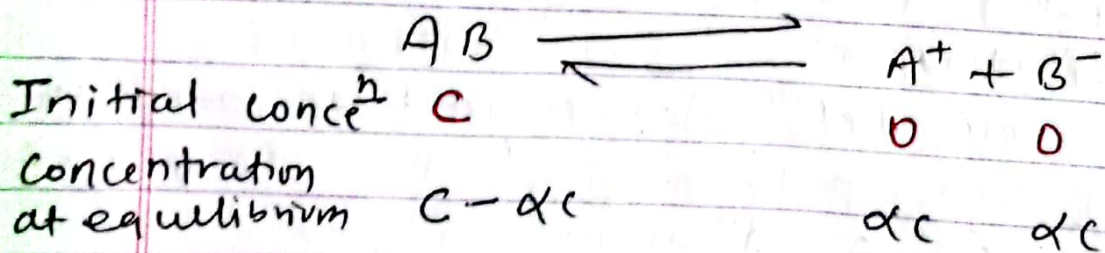
$$\alpha = \frac{\text{No. of molecules splitted into ions}}{C}$$

$$\therefore \text{no. of molecules splitted into ions} = \alpha C$$

Consider AB be an electrolyte and α be the degree of ionization.

$$\alpha = \frac{\text{Number of molecule ionized}}{\text{Total no. of molecule dissolved.}}$$

Consider AB be an electrolyte and α is the degree of ionization of the electrolyte having concⁿ 'C'. The ionization takes place as



Applying law of mass action, ionization or dissociation constant K is written as,

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

$$\therefore K = \frac{\alpha c \cdot \alpha c}{c(1-\alpha)} \quad \cdot c - c\alpha = c(1-\alpha)$$

$$K = \frac{\alpha^2 c}{1-\alpha} \quad \text{--- (1)}$$

Where K is ionization constant.

eqn (1) represents the mathematical form of Ostwald's dilution law. in terms of ~~Again~~ concentration.

If 1 mole of an electrolyte is dissolved in V litres of solution, then

$$C = \frac{1}{V}$$

Now, substituting the value of C in equation (1) we get.

$$K = \frac{\alpha^2}{(1-\alpha)V} \quad \text{--- (II)}$$

eqn (II) represents the variation of degree of dissociation of an electrolyte with dilution and is known as Ostwald's dilution law.

special cases

(a) Case-I for weak electrolyte
 $(1-\alpha)$ is almost equal to 1.

because electrolyte is weakly ionized. so α is small.

α is ~~small~~ very small.

So eqn (II) becomes,

$$K = \frac{\alpha^2}{V}$$

$$\alpha = \sqrt{KV} \quad \text{--- (III)}$$

$$\text{or } \alpha = \sqrt{\frac{K}{c}} \quad \text{--- (IV)} \quad \left[\because V = \frac{1}{c} \right]$$

Eqn (III) & (IV) is the Ostwald's dilution law for weak electrolyte.

According to this, relation (III) & (IV) the degree of ionization increases with increase in dilution. If concentration decreases the degree of dissociation increases.

(b) For strong electrolyte.

The value of α is large. So eq

$$K = \frac{\alpha^2}{(1-\alpha)V}$$

$$\alpha^2 = KV - K\alpha V$$

$$\alpha^2 + \alpha KV - KV = 0 \quad \text{--- (V)}$$

eqn (V) is the Ostwald's dilution law for

strong electrolytes.

Limitation of Ostwald's Dilution Law.

Weak electrolyte obey Ostwald's dilution law fairly well, but strong electrolyte do not obey this law, because,

① Strong electrolyte completely ionized in dilute solution, so that, there is no dynamic equilibrium between ions and unionized molecules. Hence law of mass action cannot be applied.

② For strong electrolyte $\alpha \approx 1$
i.e. $(1-\alpha) = 0$

$$\text{i.e., } k = \frac{\alpha^2 c}{1-\alpha}$$

$$k = \frac{\alpha^2 c}{0}$$

$k = \infty$ = undetermined,

so it does not apply to strong electrolyte.

(Acid base concept)

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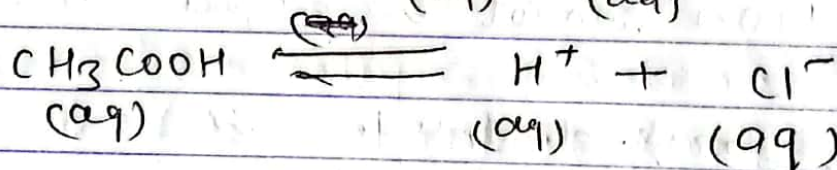
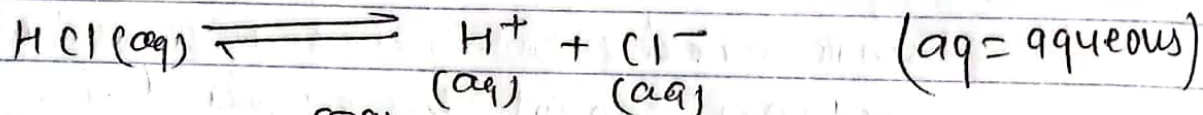
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A Arrhenius concept of acid and bases,
(Svante Arrhenius - 1887)

According to this concept,

⇒ An acid is a hydrogen containing compound that gives hydrogen ions (H^+) when dissolve in water.

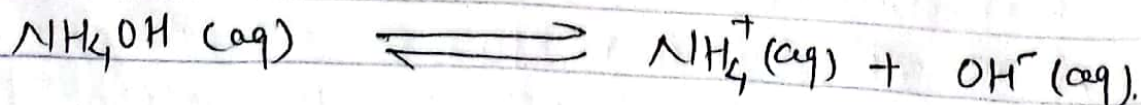
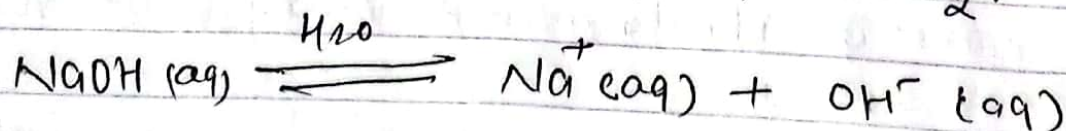
example; HCl , ~~HCl~~ , HNO_3 , H_2SO_4 ,
 CH_3COOH , H_3PO_4 etc.



⇒ Base :- A base is hydroxyl group-containing compound that gives hydroxyl ion (OH^-) when dissolve in water.

example,

$NaOH$, KOH , NH_4OH , $Ca(OH)_2$.



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According to Arrhenius concept, the neutralization reaction between acid and base is the process in which there is the union of H^+ ion from acid and OH^- ion from base to produce unionized water.



Limitation of Arrhenius concept of acid and base

This theory is applicable to aqueous solution only, but fails to explain acids and bases other than aqueous solution.

Nature of H^+ ion and OH^- ion :-

It explains H^+ ion in aqueous solution is in free state but in actual practice, H^+ ion is in hydrated form and exist as a hydronium ion (H_3O^+)



Similarly, OH^- ion form complexed species

like, H_3O_2 , H_3O_3 in ~~aqueous~~ aqueous solution.

It fails to explain acidic substance without H^+ and basic substance without OH^- . e.g, CO_2 , NO_2 , SO_2 are acidic an.

~~Not~~ Without H^+ and, NH_3 , CaO , etc are basic without OH^- .

Salts like $CuSO_4$, $AlCl_3$, $FeCl_3$ are acidic without H^+ .

4.

4. This theory does not consider the role of solvent to decide of the nature and strength of acid and base. e.g. HCl act as strong acid in water but when dissolve in benzene it act as weak acid.

B. Bronsted-Lowry concept of Acid and Bases. (J. Nicolaus Bronsted 1923)
(Also called Bronsted-Lowry proton transfer theory)

⇒ According to this concept,
Acid:- An acid is species (molecule or ~~ion~~ cation) that can donate (~~the~~) proton (H^+) to other species.

An acid is proton donor species.

Base:- An acid is a species (molecule or anion) that can accept proton from acid.
proton acceptor species.

⊗ If an acid follows Bronsted-Lowry concept are called Bronsted-acid.

e.g. HCl , HNO_3 , H_3PO_4 , HCOOH , NH_4^+
 HSO_4^-

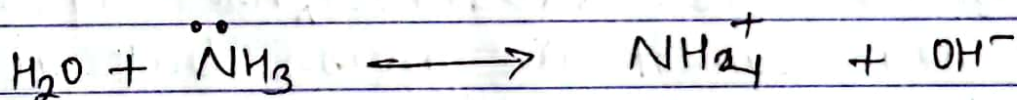
consider an example,



HCl donate proton (H^+) to H_2O , so HCl is an acid.

⊕ If an base follows Bronsted-Lowry concept are called bronsted base e.g.

NH_3 , S^{2-} , NH_2^- , Cl^- , H_2O , CO_3^{2-}

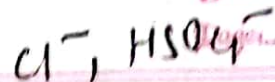


H_2O donate proton (H^+) to NH_3 . so NH_3 accepted proton act as base and H_2O act as ~~acid~~, an acid.

Merits of Bronsted concept

1). This concept is not limited to any solvent. It applies to aqueous as well as non-aqueous solvents.

ii). It can explain the basic character of



of substance like Na_2CO_3 , NH_3 etc in the absence of ~~base~~ OH^- group as they are proton acceptors.

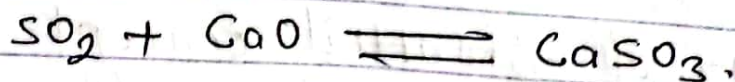
Limitations of Bronsted-Lowry concept

1. It is unable to explain about the acidic substance without proton (H^+) such as SO_2 , CO_2 , SO_3 , NO_2 , etc and basic oxides which is unable to accept ~~to~~ proton such as CaO , Na_2O , MgO , BaO etc.



2. It fails to explain about acidic behaviours of salts like AlCl_3 , BCl_3 , FeCl_3 etc. These substance ^{do not} have hydrogen and hence cannot give proton but act as acid.

3. This concept is limited to proton transfer ~~reaction~~. acid-base rxn and ignores as ~~non aqueous solvent~~ s. non proton transfer acid-base rxn.



4. Unable to explain ~~the~~ the neutralization rxn between acid and base.