# Ionic Equilibrium

Concept of Acid and Base

There are 3 type of concept of Acid and Base

a. Arrhenius concept

According to Arrhenius concept, An acid is a substance which dissociates in aqueous solution to give H^{++} ions and base is a substance which dissociates in aqueous solution to give OH^- ions.

Thus, according to them, acidic properties of substances in the solution is due to the presence of H^+ and basic properties due to the presence of OH^- ions.

For acid
$$HX \xrightleftharpoons{H_2O} H^+ + X^-$$
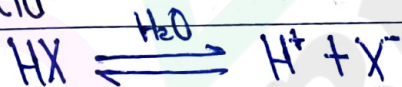
For base
$$MOH \xrightleftharpoons{H_2O} M^+ + OH^+$$

He also clearifies the strength of acid and base in term of dissociation power and classify the acid and base interms of strength.

Strong acid: Acid such as HCl, H_2SO_4, HNO_3 are completely dessociate in the solution so they are called strong acid.

Weak acid: Acid such as H_3PO_4, CH_3COOH, $HCOOH$ are feebly or partially dissociates in the aqueous solution so they are called weak acid.

Strong base: Base like NaOH, KOH are completely dissociated in aqueous solution. So they are called strong base

Weak base: Base like NH₄OH, Ca(OH)₂, Al(OH)₃ are feebly or partially dissociated in aqueous solution. So they are weak base.

Limitations of Arrhenius Concept:

→ This concept is applicable to the acid-base behaviour only in aqueous medium but can't explain in non-aqueous medium. That means that HCl gas is not acid according to this concept

→ This concept fails to explain the acidic character of CO_2, SO_2, $AlCl_3$, $FeCl_3$ as well as basic character of MgO, CaO, Na₂O etc.

2) Bronsted-Lowry concept

This theory was proposed by JN Bronsted (Denmark) and Tom Lowry (England) in 1929. This concept explains the acid-base behaviour interms of proton.

According to this concept, "An acid is a substance that can donate proton (H⁺) and base is a substance that can accept proton (H⁺).

Simply proton donor are acid and proton acceptor are base.

For E.g.

$$HCl + NH_3 \longrightarrow Cl^- + NH_4^+$$
Acid   Base
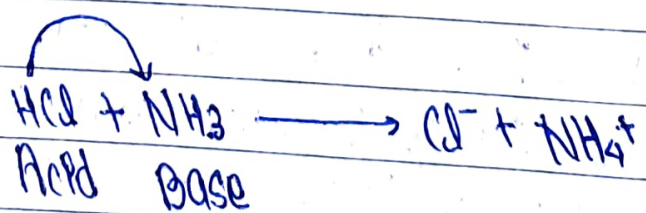
Here, HCl donate H+ and acts as acid and NH3
accept H+ from HCl and acts as base.

This theory is explained in terms of conjugate pair.

In above reaction, HCl donate proton and form Cl- ion.
Again this Cl- ion have tendency to accept proton and acts as
base. Thus a base obtained form an acid having capacity to
accept proton is called conjugate base. Here, HCl and Cl- are
conjugate acid-base pair.

Also NH3 accept proton and form
NH4+. Again this NH4+ ion have tendency to donate proton and
acts as acid. Thus, an acid obtained from a base having
capacity to donate proton is called conjugate acid. Here, NH3
and NH4+ are conjugate base-acid pair.

According to this concept, water is an
amphoteric compound which can be illustrated by the two
reaction given below:

$$H_2O + NH_3 \longrightarrow OH^- + NH_4$$
Acid   Base

$$HCl + H_2O \longrightarrow Cl^- + H_3O^+$$
Acid   Base
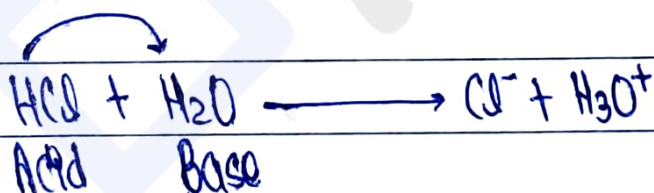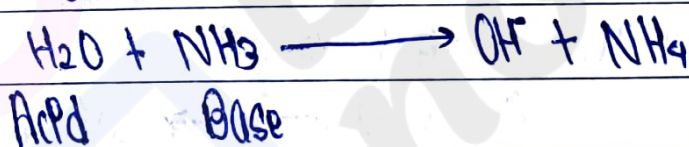
According to this concept, strength of acid and base depend
upon its tendency to donate the proton or accept the proton.

Eg. $$HCl + H_2O \rightleftharpoons Cl^- + H_2O^+$$
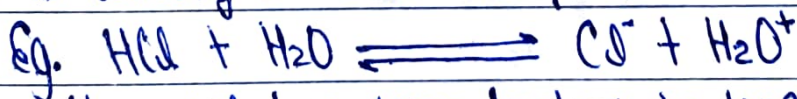
Here, HCl has strong tendency to donate proton. So, it is
strong acid but Cl- obtained from HCl has less tendency to

accept the proton. So it is weak base that means conjugate of strong acid and base is always weak and vise versa.

Advantages

i. This concept explains the basic character of the substances like Na_2CO_3, NH_3 which doesnot contain OH^- ions.

ii. ~~NH₃~~ It can explain the acid or base in aqueous as well as non-aqueous medium.

iii. This concept isn't limited to neutral molecules but also include the ionic species that acts as acid and base.

Limitation of Bronsted concept

1. This concept can explain the acidic properties of CO_2, SO_3, $AlCl_3$, BF_3 as well as basic properties of CaO, MgO, etc.

2. It cannot explain the reaction between acid and basic oxides such as SO_3, SO_2, CO_2 and MgO, CaO, etc which takes place in absence of solvent.

$$CaO + SO_3 \longrightarrow CaSO_4$$

3. Lewis Concept

Gilbert Newton Lewis in 1928 proposed a new theory regarding acid and base on the basis of electronic theory of valency.

According to this concept, "An acid is a substance that accept a lone pair of electrons through co-ordinate bond and a base is a substance that donates a pair of electron through co-ordination bond."

$$\overset{\frown}{A} + :B \longrightarrow A \longleftarrow B$$
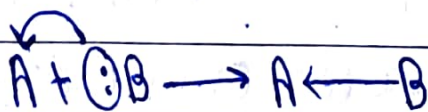
Simply acid are electron pair acceptor and base are electron pair donor.

Thus, from this concept it is evident that any unshared pair of electron containing substances are lewis base where as the substances having vacant orbital and that can accomodate pair of electrons are lewis acid.

Eg:

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}}: \longrightarrow \underset{\underset{F}{|}}{\overset{\overset{F}{|}}{B}}-F$$

Base   Acid
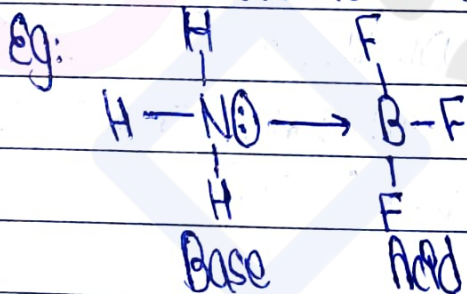
Lewis bases may be:-

(i) Negatively charged species.

Eg: Cl^-, SO_4^{--}, CO_3^{--}, etc.

(ii) Neutral molecules having unshared pairs of electrons.

Eg: NH_3, $H-\overset{..}{\underset{..}{O}}-H$, $R-OH$, $R-O-R$, etc

Since they have more electrons or electron rich species. So, lewis base are also called nucleophile.

Lewis acid may be:

i) Positively charged species.

    Eg: NH_4^+, Ca^{++}, Al^{+++}, etc.

ii) Neutral molecules having incomplete octet

    Eg: $AlCl_3$, BF_3, etc.

iii) Molecules having multiple bonds containing dessimilar electronegative atom.

    Eg: CO_2, SO_2, SO_3 etc.

Since, there is electron deficient in such species.

So, lewis acid are also called electrophiles.

Limitation:

i. This concept doesn't explain the strength of acid and base.

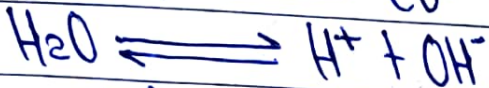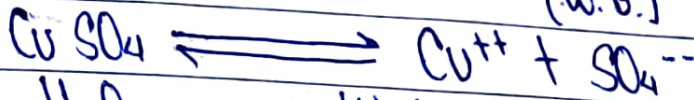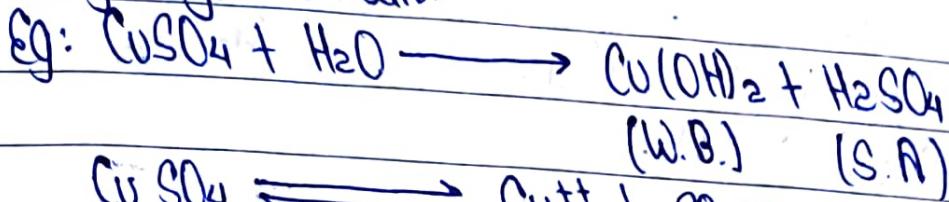ii. It doesnot explain the acid-base behaviour of substance like HCl which do not form co-ordinate covalent compound. Hence, HCl cannot be considered as lewis acid.

iii. Since, acid-base reaction are very fast but the formation of co-ordinate covalent compound is very slow. Hence, this concept doesnot fit for the acid base reaction.

Hydrolysis of salt

As we know that acid react with base to give salt and water. Some salts when dissolved in water interact with it and breakdown to its parent acid and base. This reaction is called hydrolysis of salt.

Eg: $CuSO_4 + H_2O \longrightarrow \underset{(W.B.)}{Cu(OH)_2} + \underset{(S.A)}{H_2SO_4}$

$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$

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

Simply it is defined as the interaction of ions of salt with water resulting in the formation of acid and base.

It helps to predict the nature of salt whether it is acidic or basic or neutral

Q. Predict the aqueous solution of Na_2CO_3?

Q. Why aqueous solution of $FeCl_3$ acidic?

Ans, Sodium carbonate is a salt of strong base (NaOH) and weak acid (H_2CO_3).

$Na_2CO_3 + H_2O \longrightarrow H_2CO_3 + NaOH$
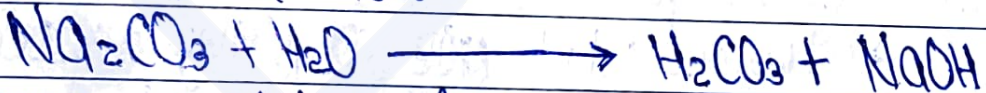
The aqueous solution of Na_2CO_3 is basic.

Ans, Aqueous solution of $FeCl_3$ is acidic because it undergoes hydrolysis and forms HCl. This strong acid release H^+ ions in the solution. Hence, the resulting solution is acidic and turns blue litmus into red.

$\underset{S.A.}{FeCl_3} + H_2O \longrightarrow HCl + \underset{W.B.}{Fe(OH)_3}$
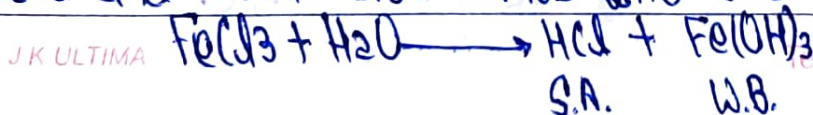
Electroolytes

The aqueous solution of chemical compound like acid, base and salt which conduct electricity at solution phase or molten state are called electrolytes. The molecules of electroolytes undergoes ionization to give charged particles (ions). Eg: HCl, H_2SO_4, $NaOH$, $Ca(OH)_2$, Na_2CO_3, $CaCl_2$, etc.

Non-Electroolytes

The aqueous solution of chemical compound which do not conduct electricity at solution state or molten state are called non-electroolytes. They undergoes molecular dissociation.

Eg: Sugar solution, kerosene, urea, etc.

Classification of electroolytes

On the basis of strength of ionization, these are two types of electroolytes.

a. **Strong electroolytes:**

Electroolytes which are completely dissociated into ions and conduct electricity easily are called strong electroolytes. Eg: HCl, H_2SO_4, $NaOH$, KOH, etc.

b. **Weak electroolytes:**

Electroolytes which are feably or partially dissociated into ions and conduct electricity partially are called weak electroolytes Eg: H_2CO_3, CH_3COOH, NH_4OH, $Ca(OH)_2$, etc.

Arrhenius theory of Ionization

In 1887, Svante Arrhenius put forward his famous theory of ionization or electrolytic dissociation. The main postulates of this theory are:-

i. Electrolytes when dissolved in water dissociates to break down into charged particles called ions. This process of breaking of molecules into ions is called Ionization.

ii. Positively charged ions are called cations and negatively charged ions are called anions and these ions are free to move in a solution.

iii. Number of cations and the number of anions are equal. So the solutions become electrically neutral.

iv. Ions have tendency to reunite to form unionised molecule so dynamic equilibrium is established between ionized and unionized molecules. This is called ionic equilibrium.

$$AB \rightleftharpoons A^+ + B^-$$

Unionised molecule   Ionised molecule
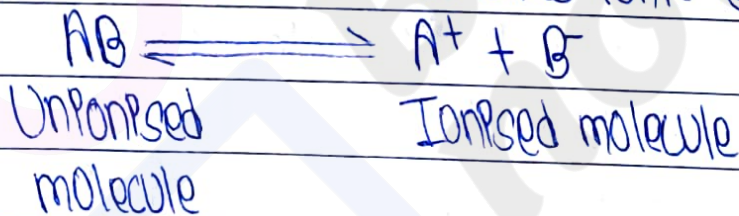
This property is characterized by the constant term called Ionization constant (k)
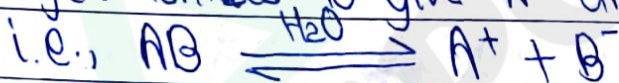
where, $k = \dfrac{|A^+| \, |B^-|}{|AB|}$

v. Properties of the electrolyte in a solution is due to the properties of the ions produced by them.

vi. Electrical conductivity is due to the migration of ions towards oppositely charged particles in a solution.

VPP. At normal condition, only a fraction of molecules ionised that means fraction of total number of molecules present as free ions in the solution is called degree of ionization which is denoted by α.

i.e., degree of ionization $(\alpha) = \dfrac{\text{no. of molecules ionized}}{\text{Total no. of molecules in a so}}$

Ionization Constant (k)

When electrolyte is dissolved in solvent, then it undergoes ionization. Let AB is the electrolyte, which is dissolved in water and gets ionized to give A^+ and B^-.
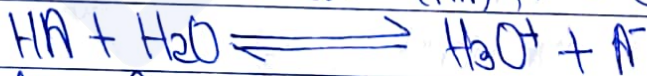
i.e., $AB \xrightleftharpoons{H_2O} A^+ + B^-$

Using law of mass action,

$$k = \dfrac{|A^+| \, |B^-|}{|AB|}$$

where, k is the ionization constant and is defined as the ratio of product of molar concentration of product to the molar concentration of reactant.

→ For aqueous solution of acid (HA), it's equilibrium is shown a

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$
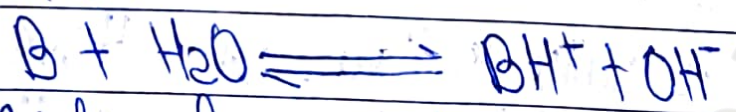
Using law of mass action,

$$K_a = \dfrac{|H_3O^+| \, |A^-|}{HA + |H_2O|}$$

where, K_a is the ionisation constant of acid.
If HA is strong acid, it is completely ionised that means more concentration of H_3O^+ is formed that means K_a is increase but

If HA is weak acid and lesser concentration of H_3O^+ is formed that K_a is decreased. Hence, it concludes that larger the value of K_a. Stronger will be the acid and vice-versa.

→ Similarly for aqueous solution of base (B), its equilibrium is shown as :-

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

Using law of mass action,

$$K_b = \frac{|BH^+| \, |OH^-|}{|B| \, |H_2O|}$$

where, K_b is the ionisation constant of base.

If B is strong base, it is completely ionised that means more concentration of OH^- is formed that means K_b is increase but if B is weak base and lesser concentration of OH^- is formed that K_b is decreased. Hence, it concludes that larger the value of K_b, stronger will be the base and vice-versa.

The reaction of number of ... into ions is called degree of ionization or degree of dissociation.

Degree of Ionization(α) = Number of molecules of electrolyte which ionize / Total number of molecules of the electrolyte

Date _____
Page _____

Degree of Ionization (α)

The number of molecules ionized to the total number of molecules in a solution is called degree of ionization.

The factors affecting the degree of ionization are

(i) Nature of electrolyte :

Strong electrolyte are completely ionised whereas weak electrolyte are partially ionised. Hence, those electrolyte which are highly ionised has high degree of ionisation.

(ii) Nature of Solvent

polarity

Ionising power depends upon dielectric constant. Higher the value of dielectric constant higher the ionising power and larger the degree of ionisation.

(iii) Temperature

Higher the temperature, longer will be the degree of ionisation. As temperature increased, molecules get vibrate and kinetic energy is increased which help to ionise the electrolyte.

(iv) Dilution

Dilution helps to reduce the interelectrons attraction of oppositely charged ion in the solution. So, when dilution increases, movement of ion is increased that means degree of ionisation is also increased.

Ostwald dilution law

This law deals with the ionization of weak electrolyte.

Ionization of weak electrolyte can be studied by the help of law of mass action and gives mathematical relationship between degree of ionization and dilution.

Ostwald dilution law state as, "an electrolyte get ionised to a larger extent with increasing the dilution at constant temperature that gives the relationship between degree of ionization and concentration of weak electrolyte.

Let us consider a weak electrolyte AB having concentration 'c' which ionized as,
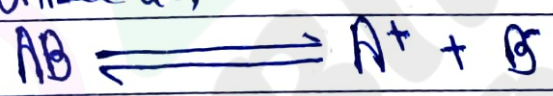
$$AB \rightleftharpoons A^+ + B^-$$

At initial   C   0   0

At equilibrium $c - c\alpha$ $c\alpha$ $c\alpha$
condition

Using law of mass action,

$$k = \frac{|A^+| \, |B^-|}{|AB|}$$

$$k = \frac{c\alpha \cdot c\alpha}{c - c\alpha}$$

$$k = \frac{\cancel{c}\alpha \cdot c\alpha}{\cancel{c}(1-\alpha)}$$

$$k = \frac{c\alpha^2}{1-\alpha}$$

where, k is the ionization constant

For weak electrolyte the degree of ionization is very low.

So, $(1-\alpha)$ is nearly equal to 1

$$So, k = c\alpha^2$$
$$\alpha^2 = \frac{k}{C}$$
$$\alpha = \sqrt{\frac{k}{C}}$$

For strong electrolyte, the degree of ionization is very high. So, $(1-\alpha)$ is 0.

$$So, k = \frac{c\alpha^2}{(1-\alpha)}$$
$$k = \frac{c\alpha^2}{0}$$
$$k = \infty$$

Hence, the value of k tends to infinity.
Therefore, Ostwald's dilution law is not applicable to strong electrolytes.

Auto-ionization of water
$$H_2O \rightleftharpoons H^+ + OH^-$$

Using law of mass action,

~~$k = \frac{H^+ + OH^-}{}$~~ $k = \frac{|H^+| |OH^-|}{|H_2O|}$

$$k \times |H_2O| = |H^+| |OH^-|$$
$$or, k_w = |H^+| |OH^-| = 1 \times 10^{-14}$$

Here, k_w is the ionization constant of water and ~~k~~

defined as the product of molar concentration of H^+ ions and OH^- ions produced by the auto-ionization of water at particular temperature. It's value 1×10^{-14} $mol^2 L^{-2}$.

Ionic product of water increase with increase in temperature due to fact that with the increase in temperature more H^+ ions and OH^- ions are formed. As a result degree of ionization is also increased and k_w also increase.

We have,
$$k_w = |H^+| \, |OH^-| = 1 \times 10^{-14} \, mol^2 \, L^{-2}$$

Since no. of $|H^+| = |OH^-|$ in water
$$|H^+|^2 = 1 \times 10^{-14} \, mol^2 \, L^{-2}$$
$$|H^+| = 1 \times 10^{-7} \, mol \, L^{-1}$$

Then, $|OH^-| = 1 \times 10^{-7} \, mol \, L^{-1}$.

Hence, the molar concentration of H^+ ions or OH^- ions is $1 \times 10^{-7} \, mol \, L^{-1}$ in pure water. If 1 to 2 drops of acid is added, the concentration of H^+ is increased, at the same time concentration of OH^- is decreased to balance the ionization constant of water. That means

i) If $|H^+| > |OH^-|$

or, $|H^+| > 1 \times 10^{-7} \, mol \, L^{-1}$

Solution is acidic

ii) If $|H^+| = |OH^-|$

$|H^+| = 1 \times 10^{-7} \, mol \, L^{-1}$

Solution is neutral

ii) If $|H^+| < |OH^-|$

$|H^+| < 1 \times 10^{-7} \, mol \, L^{-1}$

Solution is basic

Limitation of Ostwald's Dilution Law:

From Ostwald's Dilution Law,

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

For strong electrolyte, $\alpha \approx 1$

Then, $1 - \alpha = 0$

and so,

$$K_a = \infty$$

i.e., ionization constant for strong electrolyte is infinite

For weak electrolyte, $\alpha << 1$ and $1 - \alpha \approx 1$. So

$$K_{eq} = \frac{\alpha^2}{V}$$

$$\alpha^2 = K_{eq} \cdot V$$

$$\therefore \alpha = \sqrt{V}$$

Therefore, this law is not applicable for strong electrolyte or applicable only for weak electrolyte.

1. Calculate the degree of Ionization of 0.1m acetic acid having it ionisation constant $k_a = 1.8 \times 10^{-5}$.

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

$\quad (1-\alpha)c \qquad \alpha c \qquad \alpha c$

given concentration $(c) = 0.1M$

Applying law of mass action

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

$$\Rightarrow 1.8 \times 10^{-5} = \frac{\alpha c \cdot \alpha c}{(1-\alpha)c}$$
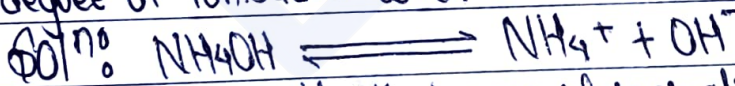
$$\Rightarrow 1.8 \times 10^{-5} = \frac{\alpha^2 c^2}{(1-\alpha)c}$$

$$\Rightarrow 1.8 \times 10^{-5} = \alpha^2 c \qquad [\because 1 >>> \alpha]$$

$$\Rightarrow \alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}}$$

×100%

$$\therefore \alpha = 0.0134$$

2. 0.1M NH_4OH solution is 1.4% ionized at 27°C. Find its degree of ionisation when it is diluted to give 10^{-4}M solution.

Soln: $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

for 0.1 M NH_4OH degree of ionization $(\alpha) = \frac{1.4}{100} = 0.014$

Applying law of mass action

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

$$\Rightarrow k_b = \frac{\alpha c \cdot \alpha c}{(1-\alpha)c}$$

Bipin Khatri

(Bipo)

Class 12 complete notes and paper collection.

Folders   Name ↑

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📁 English	📁 maths
📁 Nepali	📁 Physics

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