

Equilibrium II (Ionic Equilibrium)

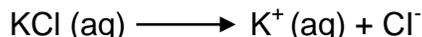
1. Classify substances as weak & strong electrolytes.
2. Classify substances as acids & Bases according to Arrhenius, Bronsted Lowry and Lewis concepts.

History:

- Michael Faraday in 1824 classified substances into electrolyte & non electrolytes on the basis of conductivity behavior of their aqueous solution.
- **Electrolytes:** - The substances which conduct electricity in their aqueous solutions were termed as electrolytes.
- While those which do not conduct electricity were termed **non electrolytes**.
- After that Arrhenius in 1880 explained that electrolytes when dissolved in water split into charged particles called ions.
- This process is called ionization or dissociation for this, he was awarded by Noble prize.

On the bases of ionization electrolytes are classified in two types.

- Strong electrolytes – the electrolytes which are almost completely ionized in solution are called strong electrolytes.



- The equation for the dissociation of strong electrolytes are written with only a single arrow directed to right.
- On the other hand, the electrolytes which are weakly ionized in their solution are called weak electrolytes.



- On the other hand equation for the dissociation of weak electrolyte are written with double arrows
- $$\text{CH}_3\text{COOH (aq)} \rightleftharpoons \text{CH}_3\text{COO}^- \text{(aq)} + \text{H}^+$$
- In case of solution of weak electrolytes the ions produced by dissociation of electrolyte are in equilibrium with undissociated molecules of the electrolyte.
 - This type of equilibrium involving ions in aqueous solution is called **ionic equilibrium**.

Ionisation of weak electrolyte.

- The fraction of total no of molecules of electrolyte dissociated that ionizes at equilibrium is called degree of ionization or degree of dissociation.
- It represents by α .
- Classify electrolytes as acids & bases for this various concepts are given

1. Arrhenius concept of acids & bases

- According to Arrhenius concept-
- **An acid** is a substance which can furnish or produce hydrogen ions (H⁺) in its aqueous solution.
- **A base** is a substance which furnish hydroxyl ions in its aqueous solution.
- Acids such as HCl, HNO₃, H₂SO₄ which are almost completely ionized are called strong acids.
- Acids such as CH₃COOH, H₂CO₃ which are weakly ionized are called weak acids.
- Similarly bases which are completely ionized in aqueous solution are called strong base. For eg. NaOH, KOH etc.

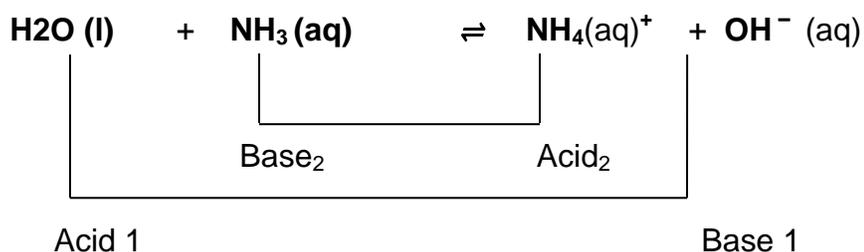
- The bases which are only slightly ionized are called weak bases eg. NH_4OH .
- H^+ ion, in an aqueous solutions is considered to be present in hydrated form in combination with water molecule as H_3O^+
 $\text{H}^+ + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+$ ion is called Hydronium ion.

2. Bronsted Lowry Concept for Acids & Bases

- In 1923, Bronsted and Lowry independently proposed new definitions for acids & base.
- They proposed that “**An acid** is a substance that can donate Proton (H^+)”.
- A base** is a substance that can accept a proton.
- In order to understand this concept of acids and bases.
- Let take some specific examples.
 $\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-$
 $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$
 $\text{H}_2\text{O} + \text{NH}_3 \rightleftharpoons \text{OH}^- + \text{NH}_4^+$
 $\text{H}_2\text{O} + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$
 Acid↑ Base↑
- From the above example, it is cleared that, A substance can act as acid only if another substance capable of accepting a proton, is present.
- These are definition are more general because according to these definitions even ions can behave as acids or bases.

Conjugate Acid- Base Pairs

An acid after losing a proton becomes a base where as a base after accepting the proton becomes an acid. For example, let us consider the reaction between water & ammonia as represented by the following equilibrium.



A base formed by the loss of proton by an acid is called **conjugate base** of the acid whereas an acid formed by the gain of a proton by the base is called **conjugate acid** of the base.

In the above reaction

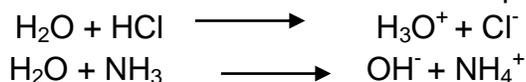
OH^- is conjugate base of H_2O & NH_4^+ is conjugate acid of NH_3

Acid base pairs such as $\text{H}_2\text{O}/\text{OH}^-$ and $\text{NH}_4^+/\text{NH}_3$ which are formed by loss or gain of a proton are called **conjugate acid-base pairs**

A strong acid would have larger tendency to donate a proton. Thus conjugate base of a strong acid would be a weak base.

Similarly conjugate base of a weak acid would be a strong base.

Substances which can act as acid as well as bases are called amphoteric, substances.



- Like H_2O when reacts with HCl it gains H^+ so it behaves as base where as when it react with NH_3 it donates H^+ to the ammonia, Here it behaves as acid. Similarly HCO_3^- NH_3

- It is quite interesting to note that both **Arrhenius** as well as Bronsted Lowry concept requires acid to be a source protons.
- Hence all Arrhenius acids are also Bronsted acids.
- However, there is a difference in the definition of bases.
- Arrhenius theory requires base to be source of OH⁻ ions in aqueous solution but
- Bronsted theory requires base to be a proton acceptor.
- Hence Arrhenius bases may not be Bronsted base.
- For e.g NaOH is a base according to the Arrhenius theory because it gives OH⁻ ions in aqueous solution but NaOH does not accept a proton as such.
- Hence it may not be classified as a base according to Bronsted theory.
- **All Arrhenius acids are Bronsted acids but all Arrhenius bases are not Bronsted bases.**
- **Limitation** – Although Bronsted Lowry theory was more general than Arrhenius theory of acids & bases.
- But it failed to explain the acid base reaction which do not involve transfer of proton.
- For eg, it fails to explain how acidic oxide such as anhydrous CO₂, SO₂, SO₃ can neutralize basic oxides such as CaO, BaO etc. even in the absence of solvent

Lewis Concept for Acids & Bases.

- G.N Lewis (1923) proposed broader and more general definition of acids & bases which do not required the presence of proton to explain the acid base behavior
- According to Lewis concept: **“An acid is a substance which can accept a pair of electrons and a base is a substance which can donate a pair a pair of electrons.”**
- Let us see some examples of Lewis acids & bases
- **Lewis bases** can be neutral molecules such as NH₃, H₂O, CH₃OH having one or more unshared pairs of electrons or anions such X⁻, OH⁻, CN⁻, NH₂⁻
- Lewis acids are the species having vacant orbitals in the valence shell of one of its atoms.
- The following species can act as Lewis acids
 - a. Molecules having an atom with incomplete octet. For example BF₃ & AlCl₃
 - b. Simple cations for eg H⁺, Na⁺, Ag⁺ etc. All cations are Lewis acids.
 - c. Molecule in which central atom has vacant orbitals and may acquire more than an octet of valence electrons.
- For eg SiF₄
- $$\text{SiF}_4 + 2 \text{F} \longrightarrow \left[\text{SiF}_6 \right]^{-2}$$
- Lewis acid Lewis base
- d. Molecule containing multiple bonds. For e.g CO₂, SO₂
- Here molecules accept lone pair of electrons from bases in their
- π antibonding molecular orbitals.
- **Acid base reactions according to this concept donation of pair of electrons by a base to a acid to form a co-ordinate bond**
- It may be noted that all Bronsted bases are Lewis bases but all Bronsted acids are not Lewis acids.
- Lewis bases contain one or more lone pairs of electrons and therefore they can also accept a proton like Bronsted base
- **Thus all Lewis bases are Bronsted bases.**
- On the other hand Bronsted acids are those which can give a proton for e.g. HCl, H₂SO₄ But they may not be capable of accepting a pair of electrons
- Hence all Bronsted acids are not Lewis acids.
- **Limitation** though Lewis Concept of acids & bases is more general than Arrhenius as well as Bronsted concepts.
- Yet ‘it has several draw backs.

- It does not help to assign the relative strength of acids & bases.
- Normally formation of co-ordination is slow. Therefore acid base reactions.
- Should also be slow but in actual practice acid base reactions are extremely fast.
- It does not explain the behavior of protonic acid such as HCl, H₂SO₄

---Module 4 of 6 Handouts Completed-----