# CONCEPTS OF ACID AND BASES

## Arrhenius Concept

### Arrhenius Acid:

Substance which gives $H^+$ ion on dissolving in water ($H^+$ donor)

**Ex.** $HNO_3$, $HClO_4$, HCl, HI, HBr, $H_2SO_4$, $H_3PO_4$ etc.

$H_3BO_3$ is not Arrhenius acid. (it is a Lewis base)

$H^+$ ion in water is extremely hydrated (in form of $H_3O^+$, $H_5O_2^+$, $H_7O_3^+$, general form $H^+ (H_2O)_n$

The structure of solid $HClO_4$ is studied by X-ray, it is found to be consisting of $H_3O^+$ and $ClO_4^-$

$$HClO_4 + H_2O \longrightarrow H_3O^+ + ClO_4^- \text{ (better representation)}$$

### Arrhenius Base:

Any substance which releases $OH^-$ (hydroxyl) ion in water ($OH^-$ ion donor) $OH^-$ ion is present also in hydrated form of $H_3O_2^-$, $H_7O_4^-$, $H_5O_3^-$.

general form $OH^- (H_2O)_n$ First group elements (except Li.) form strong bases

### Limitation of Ostwald Dilution Law

(1) It is not applicable for strong electrolyte

(2) It is not applicable for saturated solution.

### Modified Arrhenius Concept

It rectifies most of the above limitations

(i) Water is weak electrolyte and ionizes to a very weak extent.

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

$$H^+ + H_2O \longrightarrow H_3O^+$$

$$H_2O + H_2O \longrightarrow H_3O^+ + OH^-$$

Above reaction is called Autoionization or salinization of water.

(ii) Water is neutral in nature i.e.,

$$[H_3O^+] = [OH^-]$$

(iii) The substances which increase the $H_3O^+$ ion concentration act as acids and while those which increase $OH^-$ ion concentration act as bases.

**Ex.**

(a) $SO_2 + H_2O \longrightarrow \underset{\text{Acid}}{H_2SO_3} \longrightarrow H_3O^+ + HSO_3^-$

(b) $NH_3 + H_2O \longrightarrow \underset{\text{Base}}{NH_4OH} \longrightarrow NH_4^+ + OH^-$

## Basicity or Precocity of an Acid

**Types of Bases**

Mono acidic base
- ➢ Gives single $OH^-$ per molecule
  e.g. CsOH, RbOH
  $NH_4OH$

Di acidic base
- ➢ Gives two $OH^-$ per molecule
  e.g. Ba $(OH)_2$,
  Ca $(OH)_2$

Tri acidic basic
- ➢ Gives three $OH^-$ per molecule
  e.g. Fe $(OH)_3$

It is number of $H^+$ ions furnished by a molecule of an acid. An acid may be classified according to its basicity.

Thus we may have,

(i) Mono basic or Mono protic acids like HCl, $HNO_3$, $CH_3COOH$, HCN etc.

(ii) Dibasic or Diprotic acids like, $H_2SO_4$, $H_2CO_3$, $H_2SO_3$, $H_2S$ etc.

(iii) Tribasic or Triprotic acids like $H_3PO_4$, $H_3AsO_4$ etc.

## Acidity or Hydroxide of a Base

**Types of Acids**

Mono basic acid
- ➢ Gives single $H^+$ per molecule
  e.g., HA ($HNO_3$,
  $HClO_4$, HCl)

Di basic acid
- ➢ Gives two $H^+$ per molecule
  e.g. $H_2A$ ($H_2SO_4$,
  $H_3PO_3$)

Tri basic acid
- ➢ Gives three $H^+$ per molecule
  e.g.$H_3A$ ($H_3PO_4$)

It may be defined as the number of $OH^-$ ions furnished by a molecule of a base.

A base can be,

(i) Mono acidic or Monohydroxy like NaOH, $NH_4OH$, AgOH etc.

(ii) Di acidic or dihydroxy like Ba $(OH)_2$, Mg $(OH)_2$, Ca $(OH)_2$, Sr $(OH)_2$ etc.

(iii) Tri acidic or trihydroxy like Fe $(OH)_3$, Al $(OH)_3$ etc.

## Strong and Weak Acids and Bases

## Strength of Acid or Base

(i) Strength of Acid or Base depends on the extent of its ionisation. Hence equilibrium constant $K_a$ or $K_b$ respectively of the following equilibria give a quantitative measurement of the strength of the acid or base.

(ii) $$HA + H_2O \longrightarrow H_3O^+ + A^-;\ K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

(iii) Similarly,

$$B + H_2O \longrightarrow BH^+ + OH^-;\ K_b = \frac{[BH^+][OH^-]}{[B]}$$ here $H_2O$ is solvent.

Amphoteric: Substances which can act as acid as well as base are known as amphoteric

$$HCl + \underset{\text{base}}{H_2O} \longrightarrow H_3O^+ + Cl^-$$

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

acid

Amphiprotic: An amphiprotic molecule or ion possesses the dual capability of donating or accepting protons, making it versatile in its role as either an acid or a base. Typical examples of amphiprotic substances encompass water, amino acids, hydrogen carbonate ions, and hydrogen sulfate ions, all characterized by the presence of hydrogen atoms and the ability to donate protons.

In an acid-base reaction, the equilibrium consistently leans towards the generation of weak acids and weak bases.

$$\underset{\text{Strong acid}}{HA} + \underset{\text{Strong base}}{H_2O} \longrightarrow \underset{\text{Weak acid}}{H_3O^+} + \underset{\text{Weak base}}{A^-}$$

In a general context, it can be stated that "The conjugate base of a strong acid tends to be a weak base, while the conjugate base of a weak acid typically becomes a strong base."

Several organic compounds containing oxygen possess the ability to receive protons, thereby allowing them to function as bases.

**Ex.**

(a) $$\underset{\text{Ethanol}}{C_2H_5\ddot{O}H} + H_2SO_4 \longrightarrow \underset{\text{(Oxonium ion)}}{\overset{+}{\underset{\cdot\cdot}{\ddot{O}}}\ C_2H_5H_2} + HSO_4^-$$

(b) $$\underset{\text{Ethyl ether}}{(C_2H_5)_2\ \ddot{O}:} + HCl \longrightarrow \underset{\text{Oxonium ion}}{(C_2H_5)\overset{+}{\ddot{O}:}\ 2} \quad H + Cl^-$$

Bronsted lowery concept does not differ appreciably from the Arrhenius theory for aqueous solution only. Autoionization or Autoproteolysis or Self ionisation

$$\underset{\text{acid}}{H_2O} + H_2O \rightarrow H_3O^+ + \underset{\text{base}}{OH^-}$$

$$\underset{\text{acid}}{NH_3} + NH_3 \rightarrow NH_4^+ + \underset{\text{base}}{NH_2^-}$$

$$\underset{\text{acid}}{H_2SO_4} + H_2SO_4 \rightarrow H_3SO_4^+ + \underset{\text{base}}{HSO4^-}$$

A limitation of the Bronsted Lowery theory is that the extent to which a dissolved substance can act as an acid or a base depends largely on the solvent.

(a) $$\underset{\text{Acid}}{HClO_4} + \underset{\text{Base}}{HF} \longrightarrow \underset{\text{Acid}}{H_2F^+} + \underset{\text{Base}}{ClO_4^-}$$ ( $HClO_4$ acts as a acid in HF)

(b) $HNO_3$ behaves as base in $HClO_4$ and HF

$$\underset{\text{(base)}}{HNO_3} + 4HF \longrightarrow \underset{\text{(acid)}}{H_3O^+} + NO_2^+ + 2HF_2^-$$

(c) Urea is weak acidic in liquid $NH_3$

$$\underset{\text{Acid}}{NH_2CONH_2} + \underset{\text{Base}}{NH_3} \longrightarrow \underset{\text{Acid}}{NH_4^+} + \underset{\text{Base}}{NH_2CONH^-}$$

**Note:** $H_2SO_4$ also acts as base in HF solvent.

## Bronsted-Lawry Concept

## Classification of Bronsted - Lowery Acids and Bases

Bronsted - Lowery acids and bases can be

(i) Molecular (ii) Cationic (iii) Anionic

| Table - 1 | | |
|---|---|---|
| **Type** | **Acid** | **Base** |
| Molecular | $HCl, HNO_3, HClO_4,$<br>$H_2SO_4, H_3PO_4,$<br>$H_2O$ etc. | $NH_3$, $N_2H_4$, Amines,<br>$H_2O$, Alcohol, Ethers etc. |
| Cationic | $NH_4^+, N_2H_5^+, PH_4^+,$<br>$Na^+, Ba^{2+}$ (All cations)<br>$[Fe(H_2O)_6]^{3+}, [Al(H_2O)_6]^{3+}$etc. | $[Fe(H_2O)_5OH]^{2+}$<br>$[Al(H_2O)_5OH]^{2+}$ etc. |
| Anionic | $HS^-, HSO_3^-, H_2PO_4^-, HSO_4^-$<br>$HCO_3^-, HPO_4^{2-}$ etc.<br>all amphiprotic anions | $Cl^-, Br^-, OH^-, HSO_4^-, CN^-$<br>$CO_3^{2-}, SO_4^{2-}, NH_3^-, CH_3COO^-$etc.<br>all anions. |

## Reactions in Non-Aqueous Solvents

(i) Organic chemistry employs solvents like C6H6, CCl4, THF (Tetrahydrofuran), DMF (N, N-dimethyl-formamide), and others. In contrast, inorganic chemistry typically investigates reactions in an aqueous environment. Nevertheless, a substantial number of non-aqueous solvents, such as Glacial acetic acid, Hydrogen halides, SO2, etc., have been introduced in the field of inorganic chemistry.

(ii) The physical properties of a solvent, including its melting point (M.P.), boiling point (B.P.), dipole moment, and dielectric constant, play a significant role in determining its behavior.

## Classification of Solvents

There are two types of solvents

**(A)** Protonic (protic) **(B)** Aprotic

## (A) Protonic or Protic Solvents

(i) They are characterized by the presence of a transferable hydrogen and the formation of "Onium" ions Autoionization taking place in them.

**Ex.** (a) $H_2O + H_2O \longrightarrow H_3O^+ + OH^-$

(b) $NH_3 + NH_3 \longrightarrow NH_4^+ + NH_2^-$

(c) $3HX \longrightarrow H_2X + HX_2^-$

(d) $2H_2SO_4 \longrightarrow H_3SO_4^+ + HSO_4^-$

(ii) Protonic solvents may be

(a) Acidic (Anhydrous sulphuric acid, liquid HF, Glacial acetic acid etc.)

(b) Basic (liquid $NH_3$)

(c) Amphiprotic ($H_2O$, proton containing anions)

## (B) Aprotic Solvents

Such solvents do not have replaceable hydrogen in them. These can be classified into three categories

(a) Non-polar or very weakly polar, no dissociated liquids, which do not solvate strongly.

**Ex.** $CCl_4$, hydrocarbons, $C_6H_6$, $C_6H_{12}$ etc.

(b) Non-ionised but strongly solvating, generally polar solvents.

**Ex.** Acetonitrile $CH_3CN$, DMF, DMSO (dimethyl sulfoxide), THF and $SO_2$.

(c) Highly polar, autoionizing solvents.

**Ex.** Inter halogen compounds ($BrF_3$, $IF_5$ and trichloro phosphine)

(a) $2\ BrF_3 \longrightarrow BrF_2^+ + BrF_4^-$

(b) $2\ IF_5 \longrightarrow IF_4^+ + IF_6^-$

(c) $2Cl_3PO \longrightarrow Cl_2PO^+ + Cl_4PO^-$

## Levelling Solvents

(i) The Bronsted-Lowry theory is applicable to acid-base reactions in non-aqueous solvents, extending its utility in distinguishing the acidity of specific acids and in titrating weak bases.

(ii) In an aqueous solvent, mineral acids seem equally potent due to their complete ionization. Water is referred to as a "levelling solvent" because it levels the strengths of all acids to a uniform level.

(iii) If, instead of an aqueous solvent, we use mineral acids in a pure acetic acid solvent (which is a less effective proton acceptor compared to water), the acids exhibit reduced strength and can be discerned from one another

**Ex.**
$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{CH_3COOH} \longrightarrow \underset{\text{Base}}{Cl^-} + \underset{\text{Acid}}{CH_3COOH_2^+}$$

In above example acetic acid and $Cl^-$ ions both compete for protons and the former being a poor proton acceptor does it much less effectively than water. Thus, HCl in acetic acid solvent appears to be a much weaker acid than that in water.

(iv) Mineral acids in acetic acid solvent follow the following order of their strengths.

$$HNO_3 < HCl < H_2SO_4 < HBr < HClO_4$$

(v) In an aqueous solution, a weak base such as acetamide or acetanilide cannot be effectively titrated with acids. However, when this weak base is dissolved in glacial acetic acid, it transforms into a strong base and becomes amenable to titration. This transformation occurs because acetic acid, which acts as a more proficient proton donor, exerts a leveling influence on the base.

## Lux - Flood Concept (1939 & 1947)

(i) The proton plays a significant role in elucidating acid-base behavior within the framework of the Bronsted-Lowry concept. Lux noted that acid-base reactions can also occur in oxide systems, even in the absence of protons.

(ii) This approach was further expanded by Flood and applied to systems that lack protons, addressing scenarios not encompassed by the Bronsted-Lowry concept.

(iii) According to this concept a base (like CaO, BaO or $Na_2O$) is an oxide ion ($O^{2-}$) donor and an acid (like $SiO_2$, $CO_2$ or $P_4O_{10}$) is an oxide ion ($O^{2-}$) acceptor.

**Ex.**

(a) $$\overset{\text{Base}}{CaO} + SiO_2 \longrightarrow \overset{\text{Acid}}{CaSiO_3}$$

(b) $6Na_2O + P_4O_{10} \longrightarrow 4Na_3PO_4$

(iv) Substances are termed amphoteric if they show a tendency of losing as well as accepting an oxide ion.

**Ex.** $ZnO, Al_2O_3, BeO, Ga_2O_3$

## Lewis Acids and Bases

## Lewis Concept (Electronic Concept)

- An acid is a molecule/ion which can accept an electron pair with the formation of a coordinate bond.

Acid → $e^-$ pair acceptor

**Ex.** Electron deficient molecules: $BF_3, AlCl_3$

Cations: $H^+, Fe^{2+}, Na^+$

Molecules with vacant orbitals: $SF_4, PF_3$

- A base is any molecule/ion which has a lone pair of electrons which can be donated.

Base → (One electron pair donate)

**Ex.** Molecules with lone pairs: $NH_3, PH_3, H_2O, CH_3OH$