EQUILIBRIUM

ACIDS, BASES AND SALTS

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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) $SO_2 + H_2O \longrightarrow H_2SO_3 \longrightarrow H_3O^+ + HSO_3^-$

Acid

(b) $NH_3 + H_2O \longrightarrow NH_4OH \longrightarrow NH_4^+ + OH^-$

Base

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 Hydroxity 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.

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

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

base

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

acid

Amphiprotic: An amphiprotic molecule (or ion) can either donate or accept a proton, thus acting either as an acid or a base. Water, amino acids, hydrogen carbonate ions and hydrogen sulfate ions are common examples of amphiprotic species. Since they can donate a proton, all amphiprotic substances contain a hydrogen atom.

An acid–base reaction always proceeds in the direction of formation of the weak acid and the weak base. In the equilibrium,

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

In general "The conjugate base of a strong acid is always a weak base and the conjugate base of a weak acid is always a strong base."

A number of organic compounds containing oxygen, can accept protons and thus act as bases.

Ex.

(a) $$\underset{\text{Ethanol}}{C_2H_5\ddot{O}H} + H_2SO_4 \longrightarrow \underset{\text{(Oxonium ion)}}{\overset{+}{\ddot{\underset{\cdot\cdot}{O}}}\, C_2H_5\, H_2} + HSO_4^-$$

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

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

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

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

(c) Urea is weak acidic in liquid NH_3

$$NH_2CONH_2 + NH_3 \longrightarrow NH_4^+ + NH_2CONH^-$$
Acid Base Acid Base

Note: H_2SO_4 also acts as base in HF solvent.

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

Reactions in Non-Aqueous Solvents

(i) Solvents like C_6H_6, CCl_4, THF (Tetrahydrofuran), DMF (N, N-dimethyl formamide) etc. are used in organic chemistry. In inorganic chemistry reactions are generally studied in water. However a large number of non–aqueous solvents (such as Glacial acetic acid, Hydrogen halides, SO_2 etc.) have been introduced in inorganic chemistry.

(ii) The physical properties of a solvent such as M.P., B.P., Dipole moment and Dielectric constant are of importance in deciding its behaviour.

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 - Lowery theory can be extended to acid - base reactions in non-aqueous solvents. It can be used in differentiating the acid strength of a particular acid and in titration of weak bases.

(ii) In water solvent, mineral acids appear to be equally strong because of their complete ionisation, water is called here a levelling solvent because it levels all the acids to the same strength.

(iii) If instead of water solvent, we take mineral acids in pure acetic acid solvent (which is poor proton acceptor as compared to water) it is found acids become weak and can be differentiated.

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) A weak base like acetamide or acetanilide in aqueous medium cannot be titrated with acids. If however, the weak base is taken in glacial acetic acid solvent, the former behaves as a strong base and can be titrated. This is because acetic acid (which acts as a better proton donor) exerts a levelling effect on the base.

Lux - Flood Concept (1939 & 1947)*

(i) The proton plays an important role in explaining the acid-base behaviour in the Bronsted-Lowery concept. Lux observed that acid - base reactions are also feasible in oxide systems without the aid of protons.

(ii) Above approach was extended by Flood and applied to non-protonic systems, which were not covered by the Bronsted Lowery 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. Base Acid

(a) $CaO + SiO_2 \longrightarrow CaSiO_3$

(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 Concept (Electronic Concept)

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

  Acid $\rightarrow$ 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 $\rightarrow$ (One electron pair donate)

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