

## 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  $ClO_4^-$



#### 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

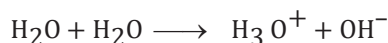
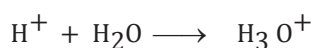
### Limitation of Ostwald Dilution Law

- (1) It is not applicable for strong electrolyte
- (2) It is not applicable for saturated solution.

### Modified Arrhenius Concept

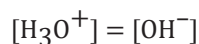
It rectifies most of the above limitations

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



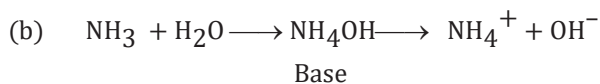
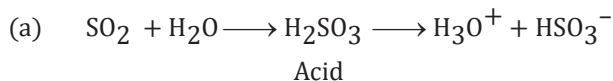
Above reaction is called Autoionization or salinization of water.

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

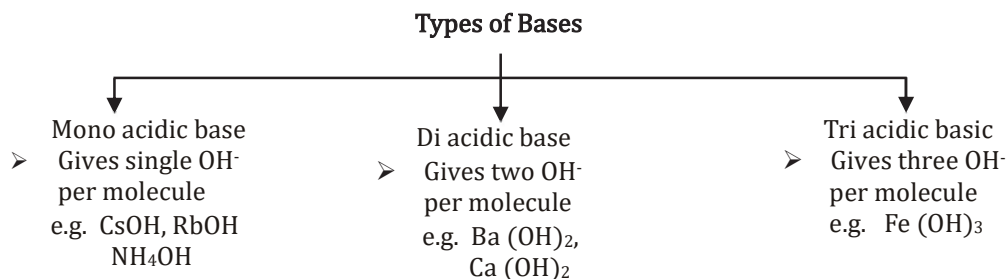


- (iii) The substances which increase the  $H_3O^+$  ion concentration act as acids and while those which increase  $OH^-$  ion concentration act as bases.

**Ex.**



## Basicity or Precocity of an Acid

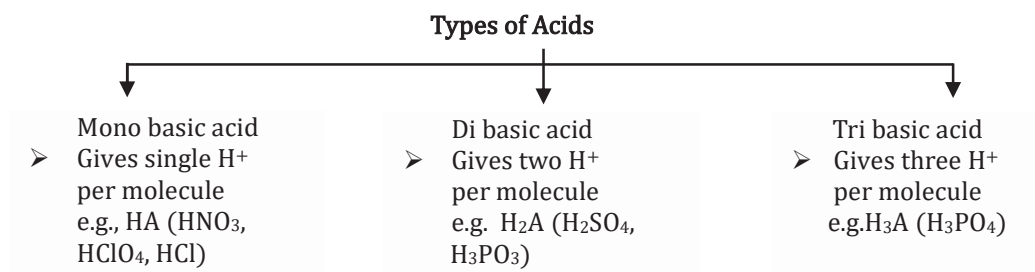


It is number of  $\text{H}^+$  ions furnished by a molecule of an acid. An acid may be classified according to its basicity.

Thus we may have,

- (i) Mono basic or Mono protic acids like  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{HCN}$  etc.
- (ii) Dibasic or Diprotic acids like,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{S}$  etc.
- (iii) Tribasic or Triprotic acids like  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{AsO}_4$  etc.

## Acidity or Hydroxide of a Base



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

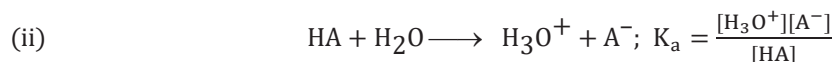
A base can be,

- (i) Mono acidic or Monohydroxy like  $\text{NaOH}$ ,  $\text{NH}_4\text{OH}$ ,  $\text{AgOH}$  etc.
- (ii) Di acidic or dihydroxy like  $\text{Ba}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$  etc.
- (iii) Tri acidic or trihydroxy like  $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$  etc.

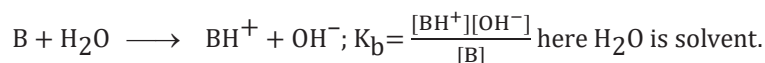
## Strong and Weak Acids and Bases

### Strength of Acid or Base

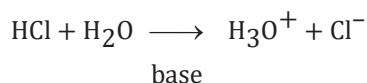
- (i) Strength of Acid or Base depends on the extent of its ionisation. Hence equilibrium constant  $K_a$  or  $K_b$  respectively of the following equilibria give a quantitative measurement of the strength of the acid or base.

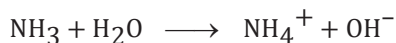


- (iii) Similarly,



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

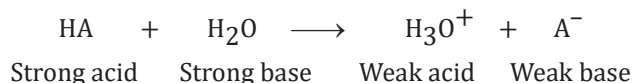




acid

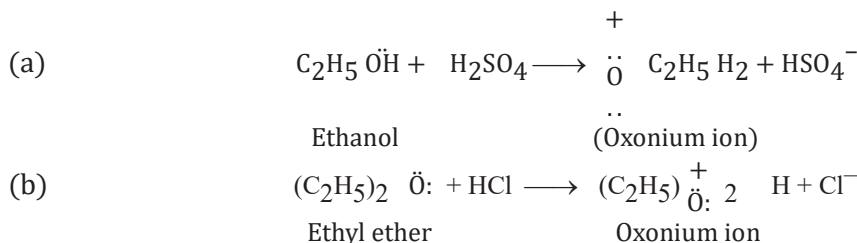
**Amphiprotic:** An amphiprotic molecule or ion possesses the dual capability of donating or accepting protons, making it versatile in its role as either an acid or a base. Typical examples of amphiprotic substances encompass water, amino acids, hydrogen carbonate ions, and hydrogen sulfate ions, all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

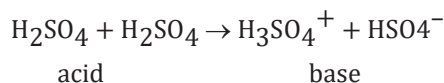
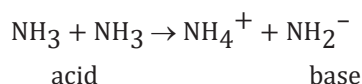
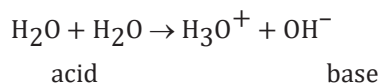


In a general context, it can be stated that "The conjugate base of a strong acid tends to be a weak base, while the conjugate base of a weak acid typically becomes a strong base."

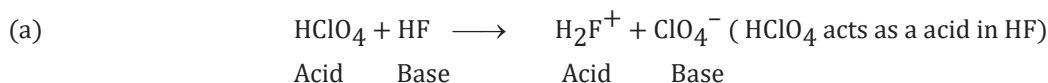
Several organic compounds containing oxygen possess the ability to receive protons, thereby allowing them to function as bases.

**Ex.**

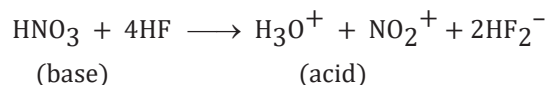
Bronsted Lowry concept does not differ appreciably from the Arrhenius theory for aqueous solution only. Autoionization or Autoproteolysis or Self ionisation



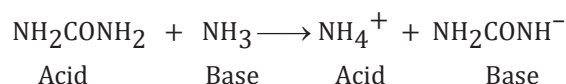
A limitation of the Bronsted Lowry theory is that the extent to which a dissolved substance can act as an acid or a base depends largely on the solvent.



(b)  $\text{HNO}_3$  behaves as base in  $\text{HClO}_4$  and HF



(c) Urea is weak acidic in liquid  $\text{NH}_3$



**Note:**  $\text{H}_2\text{SO}_4$  also acts as base in HF solvent.

**Bronsted-Lowry Concept****Classification of Bronsted - Lowry Acids and Bases**

Bronsted - Lowry acids and bases can be

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

Table - 1		
Type	Acid	Base
Molecular	HCl, HNO <sub>3</sub> , HClO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , H <sub>3</sub> PO <sub>4</sub> , H <sub>2</sub> O etc.	NH <sub>3</sub> , N <sub>2</sub> H <sub>4</sub> , Amines, H <sub>2</sub> O, Alcohol, Ethers etc.
Cationic	NH <sub>4</sub> <sup>+</sup> , N <sub>2</sub> H <sub>5</sub> <sup>+</sup> , PH <sub>4</sub> <sup>+</sup> , Na <sup>+</sup> , Ba <sup>2+</sup> (All cations) [Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> , [Al(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> etc.	[Fe(H <sub>2</sub> O) <sub>5</sub> OH] <sup>2+</sup> [Al(H <sub>2</sub> O) <sub>5</sub> OH] <sup>2+</sup> etc.
Anionic	HS <sup>-</sup> , HSO <sub>3</sub> <sup>-</sup> , H <sub>2</sub> P O <sub>4</sub> <sup>-</sup> , HSO <sub>4</sub> <sup>-</sup> HCO <sub>3</sub> <sup>-</sup> , HPO <sub>4</sub> <sup>2-</sup> etc. all amphoteric anions	Cl <sup>-</sup> , Br <sup>-</sup> , OH <sup>-</sup> , HSO <sub>4</sub> <sup>-</sup> , CN <sup>-</sup> CO <sub>3</sub> <sup>2-</sup> , SO <sub>4</sub> <sup>2-</sup> , NH <sub>3</sub> <sup>-</sup> , CH <sub>3</sub> COO <sup>-</sup> etc. all anions.

**Reactions in Non-Aqueous Solvents**

- (i) Organic chemistry employs solvents like C<sub>6</sub>H<sub>6</sub>, CCl<sub>4</sub>, 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, SO<sub>2</sub>, 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.

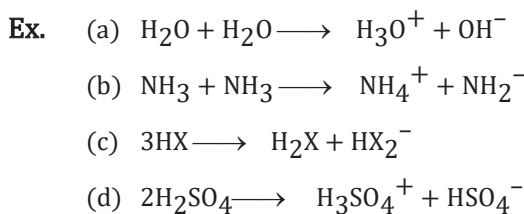
**Classification of Solvents**

There are two types of solvents

- (A) Protic (protic)      (B) Aprotic

**(A) Protic 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.



- (ii) Protic solvents may be

- (a) Acidic (Anhydrous sulphuric acid, liquid HF, Glacial acetic acid etc.)  
 (b) Basic (liquid NH<sub>3</sub>)  
 (c) Amphoteric (H<sub>2</sub>O, 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.

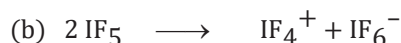
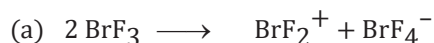
**Ex.**  $\text{CCl}_4$ , hydrocarbons,  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_{12}$  etc.

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

**Ex.** Acetonitrile  $\text{CH}_3\text{CN}$ , DMF, DMSO (dimethyl sulfoxide), THF and  $\text{SO}_2$ .

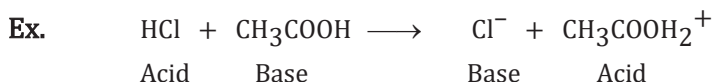
- (c) Highly polar, autoionizing solvents.

**Ex.** Inter halogen compounds ( $\text{BrF}_3$ ,  $\text{IF}_5$  and trichloro phosphine)



### 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



In above example acetic acid and  $\text{Cl}^-$  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.

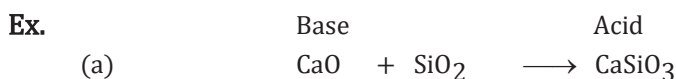
- (iv) Mineral acids in acetic acid solvent follow the following order of their strengths.

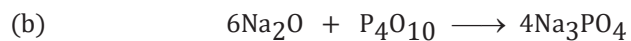


- (v) In an aqueous solution, a weak base such as acetamide or acetanilide cannot be effectively titrated with acids. However, when this weak base is dissolved in glacial acetic acid, it transforms into a strong base and becomes amenable to titration. This transformation occurs because acetic acid, which 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  $\text{CaO}$ ,  $\text{BaO}$  or  $\text{Na}_2\text{O}$ ) is an oxide ion ( $\text{O}^{2-}$ ) donor and an acid (like  $\text{SiO}_2$ ,  $\text{CO}_2$  or  $\text{P}_4\text{O}_{10}$ ) is an oxide ion ( $\text{O}^{2-}$ ) acceptor.





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

**Ex.**  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{BeO}$ ,  $\text{Ga}_2\text{O}_3$

### 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  $\rightarrow$   $e^-$  pair acceptor

**Ex.** Electron deficient molecules:  $\text{BF}_3$ ,  $\text{AlCl}_3$

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

Molecules with vacant orbitals:  $\text{SF}_4$ ,  $\text{PF}_3$

- 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:  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$