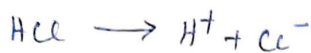


Concepts of Acids and Bases

(A) Arrhenius concept of Acid and Base:-

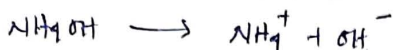
According to Arrhenius, i) An acid is a substance that furnishes H^+ ions in aqueous solution.

Ex:-



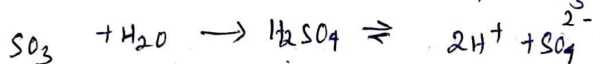
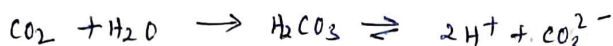
(ii) A base is a substance which furnishes OH^- in aqueous solution.

Ex:-

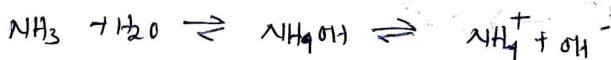
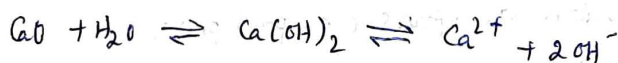


Application of Arrhenius concept:-

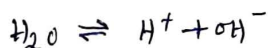
(i) It explains the acidic nature of aqueous solution of non-metallic oxides e.g. CO_2 , SO_2 , SO_3 , N_2O , N_2O_5 , P_2O_3 etc.



(ii) It explains the basic nature of aqueous solutions of several substances like metal hydroxides. e.g. CaO , MgO , NH_3 , N_2H_4 etc.

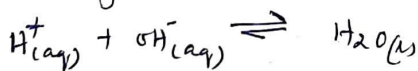


(iii) Water is amphoteric in nature as it furnishes both H^+ and OH^- in aqueous solution.



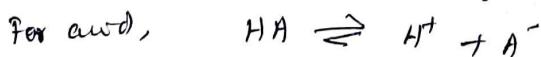
(iv) Neutralisation reaction:-

Basically it is a reaction between H^+ and OH^- to form H_2O



(v) Strength of Acid/Base:-

It depends upon the tendency of acid or base to furnish H^+ or OH^- in solution and can be determined by applying laws of equilibrium.



$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Higher is the value of K_a , more is the concentration of H^+ and so stronger is the acid.



$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

Higher is the value of K_b , more is the concⁿ of OH^- and so stronger is the base.

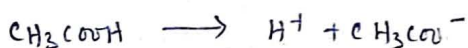
Limitations of Arrhenious Theory:-

- (i) It fails to explain the behaviour of acids and bases in non-aqueous solution. eg. dry HCl should not act as acid, but it act as acid.
- (ii) It fails to explain the neutralization reactions giving rise to salt formation in absence of solvent. eg.
- $$\text{CO}_2 + \text{CaO} \rightarrow \text{CaCO}_3$$
- $$\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s)$$
- (iii) It fails to explain the acidic character of certain salt eg. AlCl_3 , BF_3 etc. and basic character of NH_3 , PH_3 etc. in absence of aqueous medium.
- (iv) It fails to explain the fact that H^+ ion exist in water as H_3O^+ i.e. hydronium ion. Since H^+ is the simplest and smallest ion and thus posses strong tendency to get hydrated.

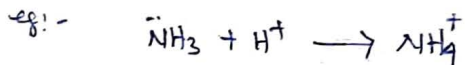
Bronsted - Lowry concept:-

According to this concept:-

- (i) Acids are proton donors i.e. protogenic substances.



- (ii) Bases are proton acceptors i.e. protophiles.

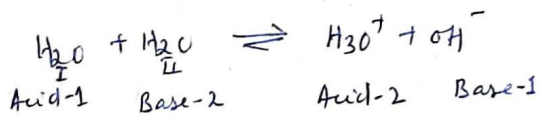


The proton donated by an acid is not capable to exist in free state and always gets solvated, eg.



Amphoteric or amphiprotic substance:-

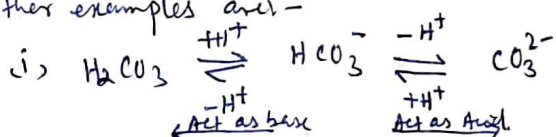
A substance, which is capable of both donating and accepting the proton and water is the best example.

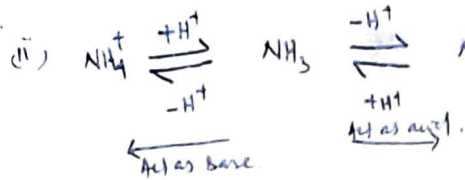


In forward reaction first molecule of H_2O , donates H^+ to second molecule of H_2O , so I is Bronsted acid and II is Bronsted base.

In backward reaction H_3O^+ donates proton to OH^- , so H_3O^+ is acid and OH^- is base.

other examples are-





Types of Bronsted acids:-

A molecule, cation or anion may act as Bronsted acid.

(i) Molecular acids:- $\text{HCl}, \text{HNO}_3, \text{HCl}, \text{H}_2\text{SO}_4, \text{H}_3\text{PO}_4, \text{CH}_3\text{COOH}, \text{H}_2\text{O}$ etc.

(ii) Cations:- $\text{NH}_4^+, \text{N}_2\text{H}_5^+, \text{H}_3\text{O}^+$ etc.

(iii) Anions:- $\text{HCO}_3^-, \text{HSO}_4^-, \text{H}_2\text{PO}_4^-, \text{HPO}_4^{2-}, \text{HS}^-$ etc.

Types of Bronsted bases:-

They also may be molecules, cations or anion.

(i) Molecular:- $\text{NH}_3, \text{N}_2\text{H}_4, \text{PH}_3, \text{RNH}_2, \text{ROH}$ etc.

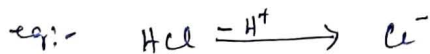
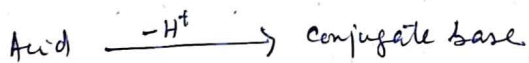
(ii) Cations:- $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}, [\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ etc.

(iii) Anions:- $\text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{OH}^-, \text{HS}^-, \text{CN}^-, \text{CO}_3^{2-}, \text{NO}_3^-, \text{SO}_4^{2-}$ etc.

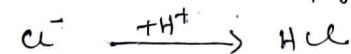
Conjugate Acid - Base pair:-

A pair of acid-base, which differ by a proton is known as conjugate acid-base pair.

Every acid has its conjugate base and every base has its conjugate acid. Conjugate base of an acid may be obtained by removal of proton (H^+) from it and conjugate acid of a base is obtained by adding H^+ in it.



Conjugate base



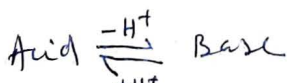
Base

Conjugate acid

All acid-base reaction involve two conjugate acid-base pairs, i.e. when an acid react with base, another acid and base are formed, and the reaction may be written as:

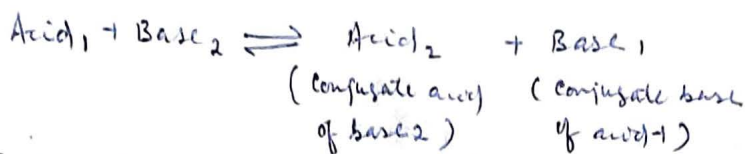


A conjugate acid / base pair differ by a proton (H^+)

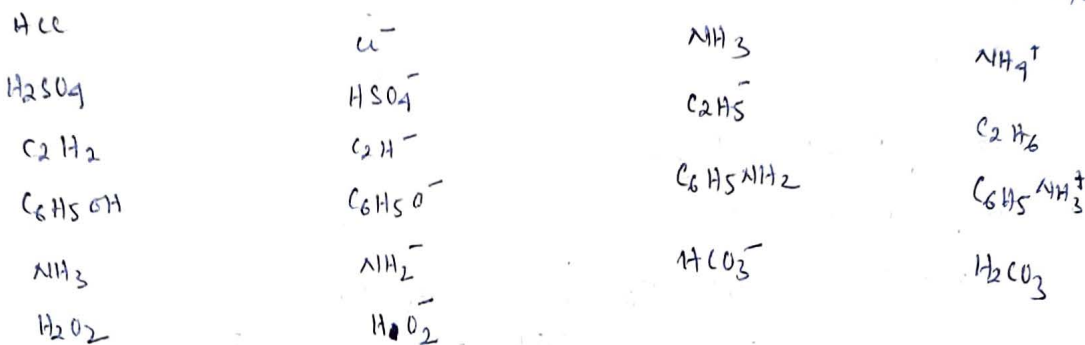
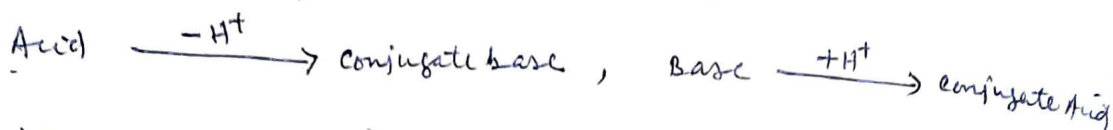


Conjugate pair

Some examples of reactions involving conjugate acid-base pair are given below.

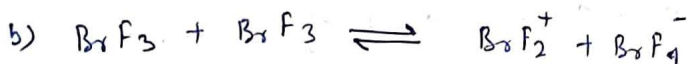
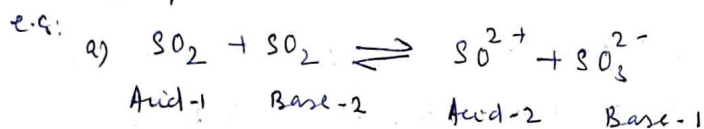


Some examples of conjugate Acid-Base pair are:-



Limitation of Bronsted Concept:-

- (i) A substance may be defined as acid or base only when it reacts with other substance.
- (ii) Some acid base reaction are known where no proton transfer takes place..

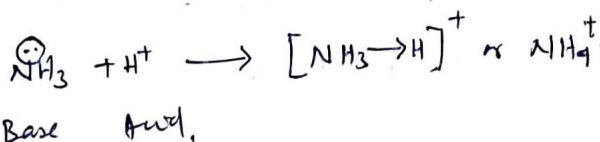
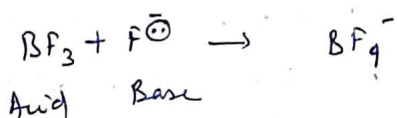


- (iii) It does not explain acid-base behaviour in non-protic solvent like COCl_2 , SO_2 , H_2O etc.

LEWIS CONCEPT OF ACID AND BASE:-

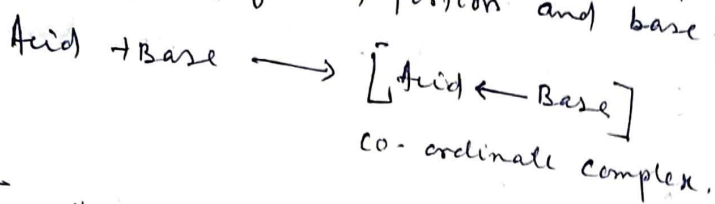
According to Lewis concept:-

- (i) An acid is electron pair acceptor i.e. electrophilic species while base is electron pair donor i.e. nucleophilic species.

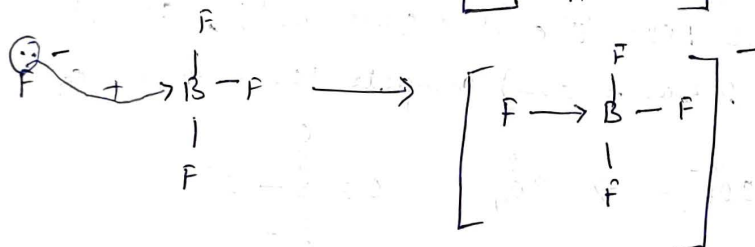
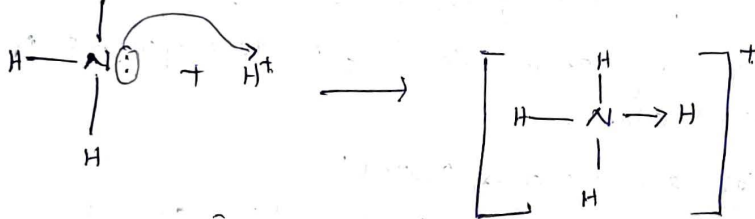
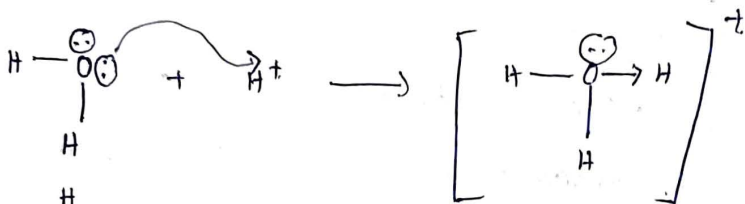
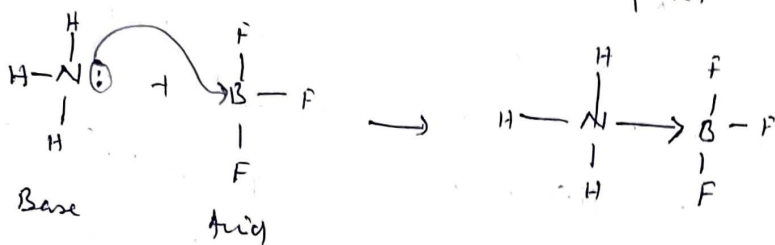


- (ii) An acid-base reaction is the sharing of electron pair between acid and base. The electron pair is made available by base.

which acts as electron pair donor (also known as ligand) while acid is acceptor. The product is co-ordinated compound, co-ordinated complex or adduct, made-up of acid portion and base portion.



Ex:



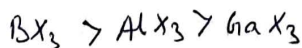
Type of Lewis Acids -

(i) Molecules with central atom having incomplete octet:

All the electron deficient molecules acts as Lewis acid e.g.

BF_3 , BCl_3 , BI_3 , AlCl_3 , GaCl_3 , BeF_2 etc. Strength of these Lewis acids increases with

- (i) an increase in nuclear charge of central atom.
- (ii) an increase in the number and relative electronegativity of atom attached to central atom e.g. $\text{SO}_2 < \text{SO}_3$.
- (iii) A decrease in radius of central atom. However some anomalies are known.



(ii) Molecules with central atoms having empty d-orbitals:-

Example:- SiX_4 , GeX_4 , TiCl_4 , PX_3 , PX_5 , SF_4 , AlF_3 , SnCl_3 , AsF_5 , SbF_5 , XeF_6 etc.

c) Cations:-

All cations are supposed to behave like Lewis acid, cations with noble gas configuration (eg. Na^+ , Mg^{2+} , Al^{3+} etc) have little affinity for electron while ions like H^+ , Ag^+ , Cu^{2+} , Fe^{3+} etc have more affinity.

Acid strength of simple cation increase with:

- increase in positive charge on the $\text{Fe}^{2+} < \text{Fe}^{3+}$
- decrease in ionic radii, $\text{K}^+ < \text{Na}^+ < \text{Li}^+$
- Increase in effective nuclear charge $\text{Li}^+ < \text{Be}^{2+} < \text{B}^{3+}$

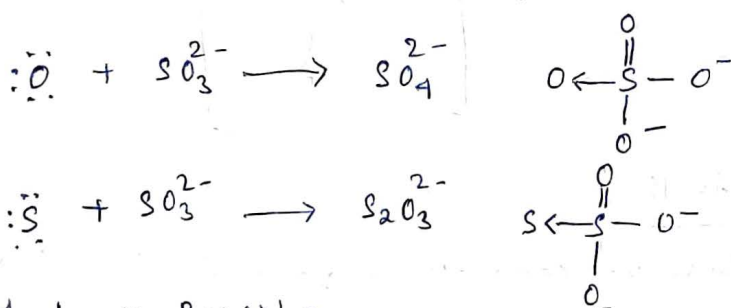
d) Molecules whose central atom is linked with more electronegative atom by double bond:-

Ex: $\text{O}=\text{C}^{\delta+}=\text{O}(\text{CO}_2)$, $\text{S}^{\delta+}=\text{O}(\text{SO}_2)$, SO_3 etc.

When Lewis base approaches the central atom, the π -electron density is shifted from central to highly electronegative surrounding atom leading to development of positive charge on central atom.

e) Elements with an electron sextet:-

Such elements like O and S (ns^2, np^4), accept electron pair from Lewis bases and complete their octet. eg.



Types of Lewis Bases:-

a) molecules having lone pair of electrons:-

eg:- Alcohols ($\text{R}-\ddot{\text{O}}-\text{H}$), amines ($\text{R}-\ddot{\text{N}}\text{H}_2$), NH_3 , PH_3 , PCl_3 , $\text{R}-\ddot{\text{O}}-\text{R}$, $\text{H}_2\ddot{\text{O}}$ etc.

b) Simple anions:-

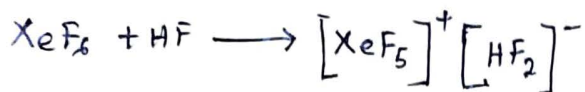
All anions behave as Lewis base eg:- OH^- , CN^- , Cl^- , Br^- , F^- , CH_3^- etc.

c) molecules containing multiple bonds:-

eg:- $\text{CH}_2=\text{CH}_2$, cyclopentadienyl anion etc.

d) Halides:-

Those halides which donate halide ions behave as Lewis bases: eg:- XeF_2 , XeF_4 , XeF_6 , Cl_2F , CoCl_2 etc.



(7)

Limitation of Lewis concept:-

- (i) It does not explain the behaviour of protonic acids such as HCl , H_2SO_4 , HNO_3 etc, which do not accept electron pair i.e. do not undergo co-ordination bonding with bases.
- (ii) It does not predict for relative strength of acids and bases.
- (iii) It is specially a general approach for co-ordination compound formation and co-ordination reaction.
- (iv) Usually co-ordination reaction are slow. It means that neutralisation of acid-base should occur slowly, but these reactions are extremely fast.
- (v) Catalytic activity of Lewis acid cannot be explained because catalytic activity of many acid is due to their tendency to furnish H^+ . Lewis acid does not do so.

————— 0 —————