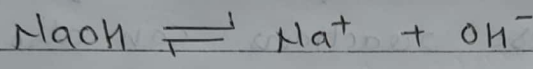
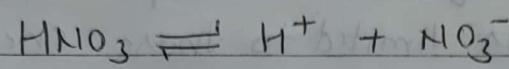


## Chapter - ACIDS AND BASES

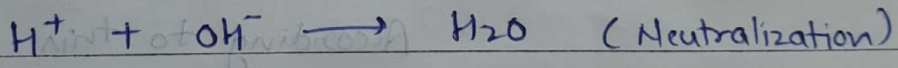
### Arrhenius Concept :-

According to this concept, an acid is any hydrogen containing compound which gives hydrogen ( $H^+$ ) ions in aqueous solution and base is that hydroxy compound which gives hydroxyl ( $OH^-$ ) ions in aqueous solution.



According to Arrhenius, the acidic character of an acid is due to the presence of  $H^+$  ions and basic character of a base is due to the presence of  $OH^-$  ions.

In the neutralization process  $H^+$  ions of the acid combine with  $OH^-$  ions of the base to form water.



### Limitations -

- (1) On the basis of this concept, acids and bases have been defined in terms of aqueous solutions. This definition is applicable for hydrogen and hydroxyl compounds. For example -  $HCl$  is regarded as an acid when dissolved in water. It does not act as an acid in the gaseous form or when dissolved in ~~water~~ some other solvent.

(2) This concept does not explain the acidic and basic character of substances in non aqueous solvents.

for Example - Acidic character of Ammonium nitrate in liquid  $NH_3$  and Basic character of Sodamide could not be explained by this concept

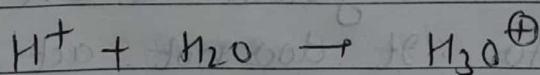
(3) on the basis of this concept, the Process of Neutralization is limited to those chemical reactions which take place in aqueous solutions. Although these reactions can also take place in other solvents and even in the absence of solvents.

Bronsted - Lowry Concept -

Bronsted and Lowry in 1923 gave Proton Exchange theory to explain the behaviour of Acids and bases.

According to this concept -

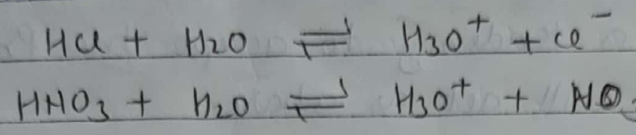
(1) Acid is regarded as a substance which gives off proton in solution. This proton is solvated i.e. it combines with one or more molecules of the solvent. In the aqueous solution, it combines with a water molecule to form  $H_3O^+$  ions which are responsible for the acidic character of an acid



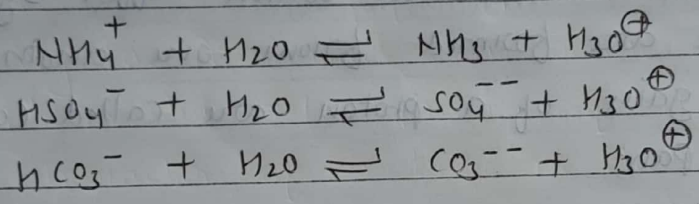
Hydronium ion

For Example -

For an acid to show its acidic properties, the presence of solvent is absolutely necessary. Dry HCl, Dry HNO<sub>3</sub> and Dry H<sub>2</sub>SO<sub>4</sub> do not show acidic properties. They develop their acidic character only in the presence of solvent.



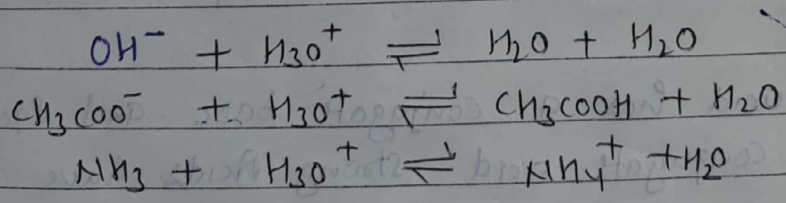
According to this concept, any neutral molecule or even an ion will be regarded as an acid so long as it can give proton in solution



NOTE - The strength of an acid depends upon the relative ease with which it can give proton in solution

(2) **Base** is regarded as a molecule or ion which can accept protons given off by an acid.

For Example -

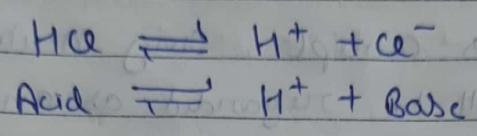


NOTE - The strength of the base depends upon the firmness with which it can hold the protons given off by an acid.

Thus on the basis of this theory acid is proton donor and base is proton acceptor

### Acid Base Relationship -

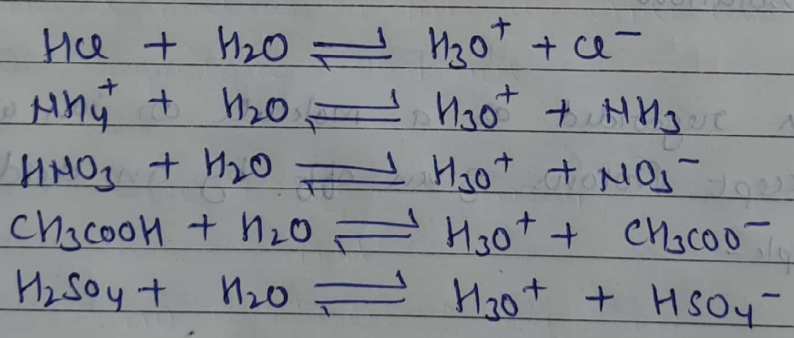
When an acid donates a proton in solution, the remaining part of its molecule which is an anion will have a tendency to accept the proton back and thus it will act as a base.



Such an acid and a base which differ by a proton and are formed from one another by loss or gain of a proton are called conjugate acid base pair

For Example -

HCl is an acid conjugate to the base  $\text{Cl}^-$   
 $\text{NH}_3$  is a base conjugate to the acid  $\text{NH}_4^+$



Thus each acid has a conjugate base and each base has a conjugate acid. Strong acids have weak conjugate bases and weak acids have strong conjugate bases.

## Advantages of Bronsted Lowry concept -

Bronsted - Lowry concept has the following advantages over Arrhenius concept

- (1) This concept is more general. According to this concept, acids and bases may be neutral molecules, positive ions or negative ions.
- (2) In this concept, the definition of acids and bases does not depend upon water or any other solvent.
- (3) On this basis of this concept, acid base reactions taking place in water or other solvents may be explained.

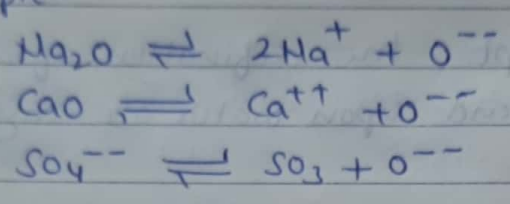
## Limitations -

- (1) This concept explains only those acid base reactions in which exchange of protons takes place. This concept could not explain the acid base reactions in which no exchange of protons takes place.
- (2) This concept explains only those acid base reactions in which solvent is present. It could not explain the acid base reactions which take place in the absence of solvent.

### LUX - FLOOD CONCEPT

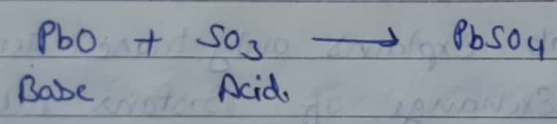
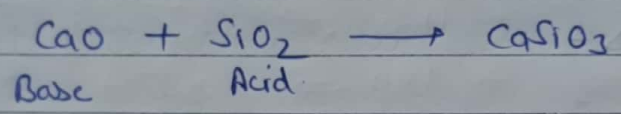
This concept was proposed by Lux and extended by Flood. According to this concept - Base is a substance which donates the oxide ion and an acid is a substance which accepts the oxide ion

For Example -

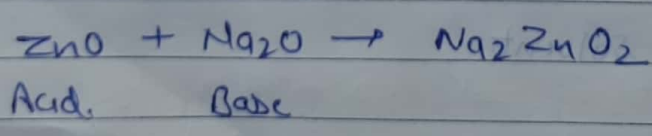
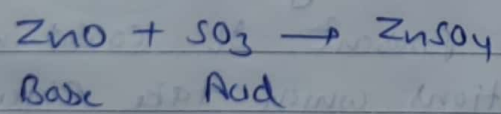


⇒ Thus Base is an oxide ion donor and an acid is an oxide ion acceptor.

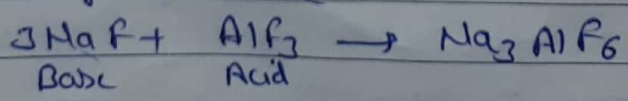
For Example -



NOTE- The substances which shows a tendency to give up as well as to take up oxide ions are known as amphoteric substances



The oxide transfer concept can be extended to include the transfer of any anion such as halide, sulphide etc.



Limitations - This concept is limited only to a few acid

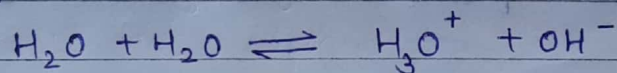
base reactions.

**The Solvent System Concept :-** This concept was proposed by franklin. It explains the acid base behaviour in aqueous and non aqueous solvents.

According to this concept an acid is a substance which, in a solvent, increases the concentration of a cation characteristic of that solvent and a base is a substance which, in a solvent, increase the concentration of anion characteristic of that solvent.

The characteristic cations and anions of the solvent are produced as a result of its auto ionization.

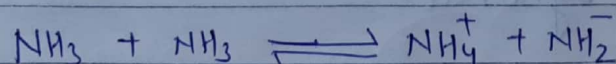
for Example - 1. The auto ionization of water is as follows -



Solvent cation      Solvent anion

1. The substances which gives  $\text{H}_3\text{O}^+$  ions in water are acids and the substances which give  $\text{OH}^-$  ions in water are bases.

2. liquid  $\text{NH}_3$ , undergoes auto ionization as -

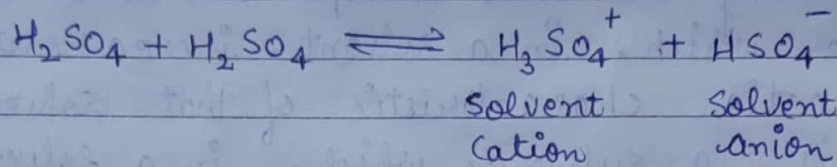
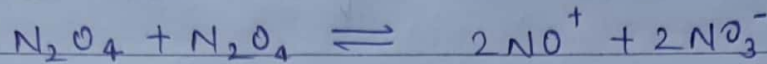


Solvent cation      Solvent Anion

The substances which give  $\text{NH}_4^+$  ions in liquid  $\text{NH}_3$  act as acids and the substances which give  $\text{NH}_2^-$  ions in liquid  $\text{NH}_3$  act as

base.

The auto ionization of some other solvent may be represent as -



Limitations :-

1. This concept explains only those acid base reactions in which solvent is present. It could not explain the acid base reaction which take place in the absence of solvent.
2. This concept does not explain the acid base reactions in which ions are absent.
3. In this concept, the chemical properties of the solvent are considered and the physical properties of the solvent are completely ignored.



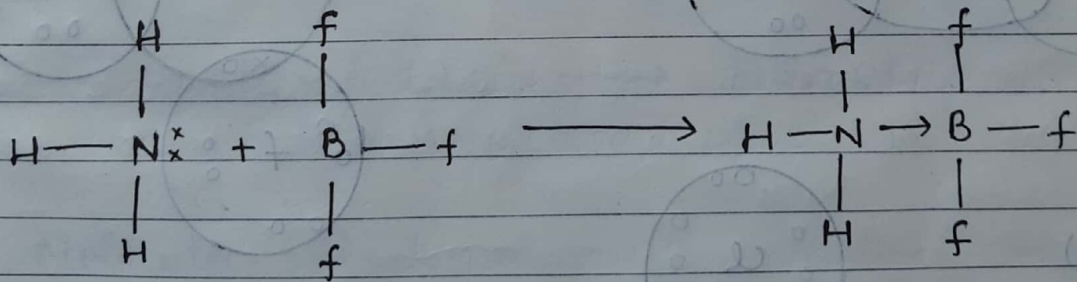
## Lewis Concept :-

L.A  $\Rightarrow$  Lewis Acid      L.B  $\Rightarrow$  Lewis Base  
 Lone Pair Acceptor      L.B = Lone Pair Donor

G.N Lewis in 1923 gave the electronic interpretation of acids and bases.

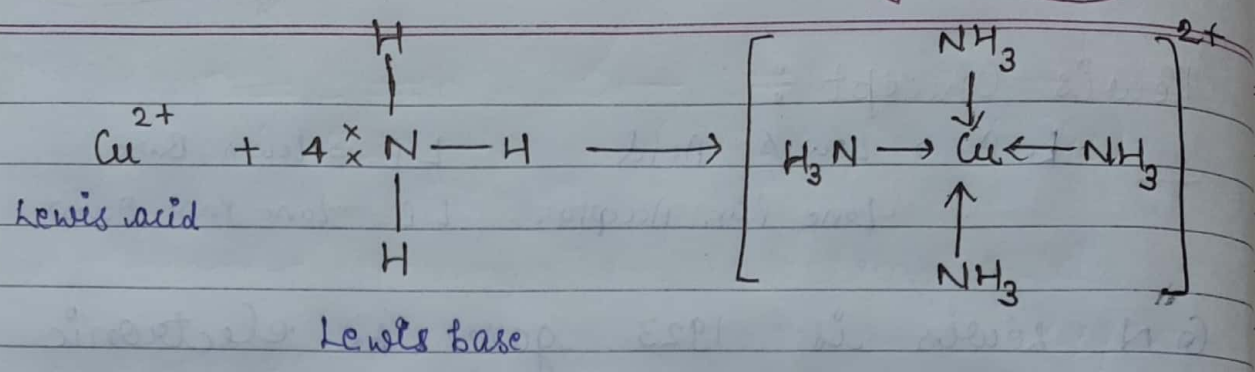
According to this concept, base is a substance which can donate lone pair of electrons and acid is a substance which can accept lone pair of electrons and the process of neutralization is simply the formation of coordinate bond between electron donor and electron acceptor systems.

for Example :- 1. nitrogen atom of ammonia donate electron pair to the boron atom of  $BF_3$  molecule. Hence,  $NH_3$  is a Lewis base and  $BF_3$  is a Lewis acid.



Lewis base      Lewis acid

2.  $NH_3$  is a Lewis base and  $Cu^{+2}$  ion is Lewis acid.



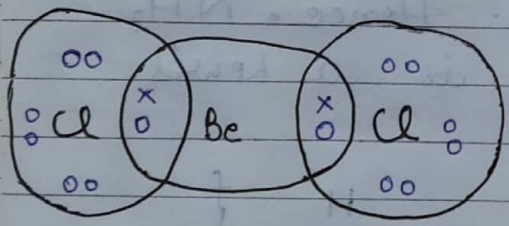
### Classification of Lewis Acid :-

(i) Molecules in which central atom has an incomplete octet :-

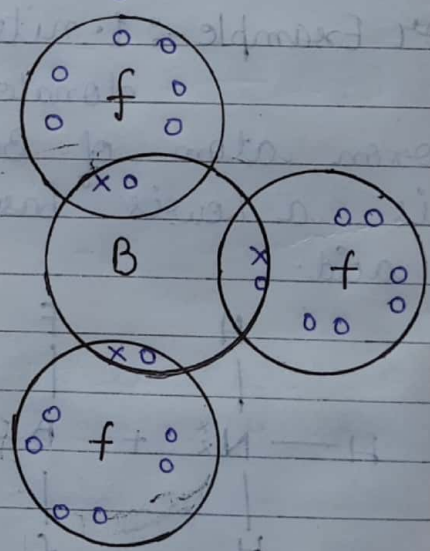
The Example of this class of acids are electron deficient molecules such as halides of Be, B and Al.

for Example :-  $\text{BeCl}_2$ ,  $\text{BF}_3$ ,  $\text{AlCl}_3$  etc.

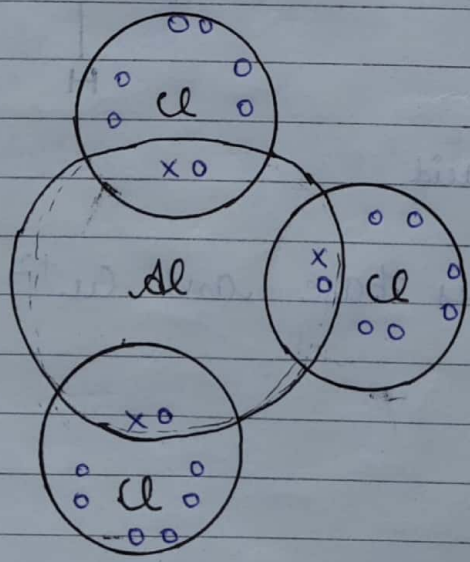
(i)



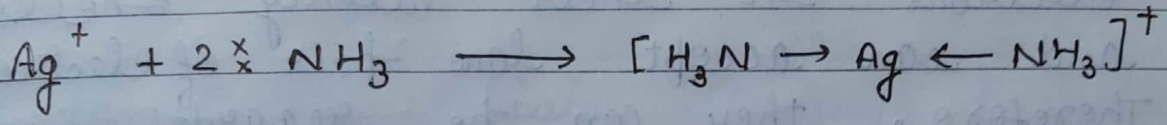
(ii)



(iii)



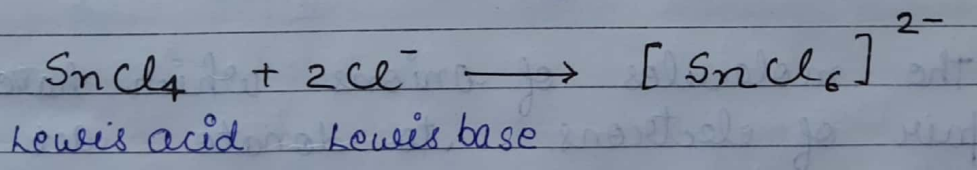
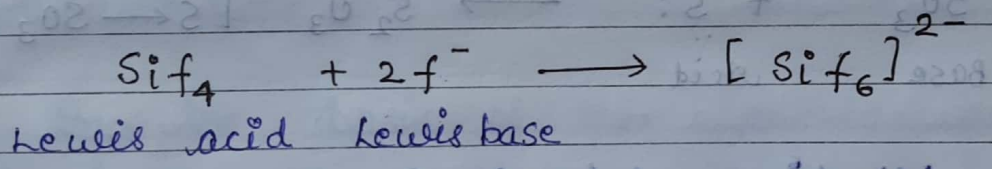
(ii) Simple Cation-: All simple cations act as Lewis acids because they have a tendency to accept the electron pairs. Small cations act as stronger Lewis acid than large cations.  $H^+$  ion is the strongest Lewis acid.



(iii) Molecules in which central atom has vacant d-orbitals -:

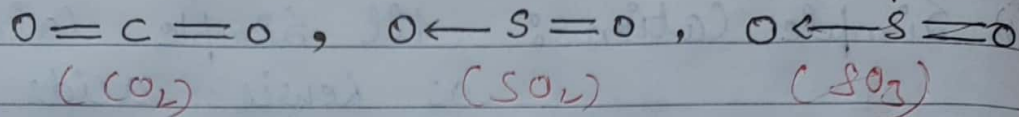
In these cases, the central atom has vacant d-orbitals to accept the lone pair of electrons.

for Example-  $SiF_4, SnCl_4, PCl_3, SF_4$  etc.

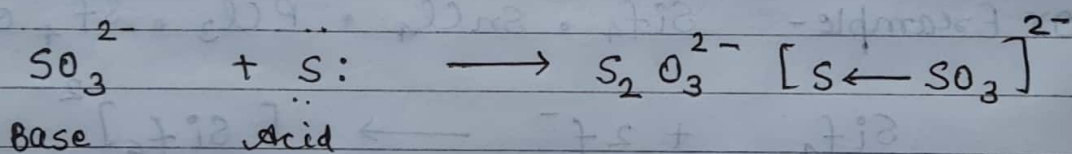
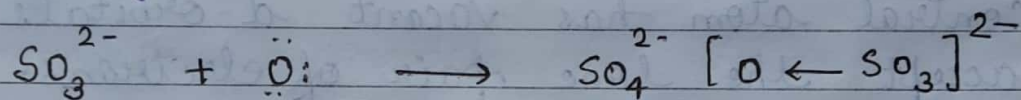


(iv) Molecules which have a multiple bond between atoms of different electronegativity -:

The Example of this class of Lewis acids are  $CO_2, SO_2, SO_3$  etc.



(v) Element having an electron sextet of Oxygen and Sulphur atoms contain six electrons in their valency shells and can accept lone pair of electrons. Therefore, they can be regarded as Lewis acids. Thus the conversion of  $\text{SO}_3^{2-}$  to  $\text{SO}_4^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  by the addition of oxygen and Sulphur respectively are acid base reactions



### Classification of Lewis Bases :-

The molecules of anions which have lone pair of electrons to donate act as Lewis bases.

for Example :-  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{F}^-$ ,  $\text{CN}^-$ ,  $\text{OH}^-$  ions act as Lewis bases.

This concept is superior to Bronsted-Lowry concept in the following respects :-

## Advantages :-

- (i) This concept is more general than Bronsted concept. In this concept, acid base behaviour does not depend on particular element or solvent.
- (ii) This concept explains the basic properties of metallic oxides and acidic properties of non-metallic oxides.
- (iii) This concept also explains those acid-base reactions in which no exchange of protons takes place.

## Limitations :-

- (i) On the basis of this concept acids and bases can not be arranged in the order of their relative strength.
- (ii) In general, acid-base reactions are fast but there are certain Lewis acid-base reactions which are slow.

## Relative Strength of Acids and Bases :-

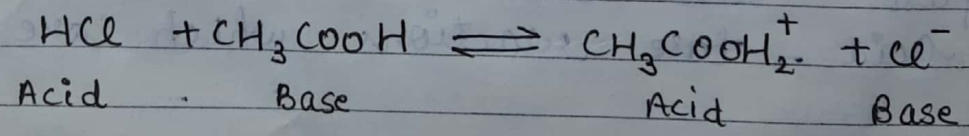
The relative strength of acids and bases depends upon the following factors:

### 1. Effect of Solvent :-

(a) Acid strength :- According to Bronsted and Lowry concept, the strength of an acid depends on the strength of the base which accepts the proton given off by an acid.

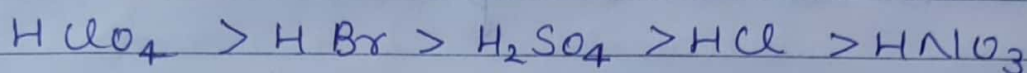
For Example :- Consider the three solvents, glacial  $\text{CH}_3\text{COOH}$ , water and liquid  $\text{NH}_3$  of increasing basic character.

(i) Acetic acid :- Although  $\text{CH}_3\text{COOH}$  is an acid, it can also accept proton to some extent and thus acts as a base. The ionization of strong acid,  $\text{HCl}$  in this medium may be represented as.

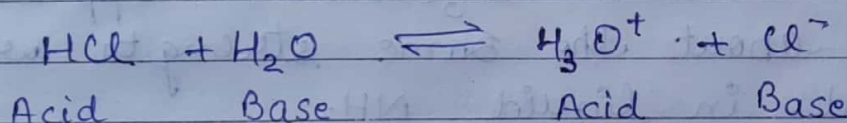


The equilibrium shifts to a little extent to the right because  $\text{CH}_3\text{COOH}$  has a small tendency to accept protons.

Thus even strong acids act as weak acids in  $\text{CH}_3\text{COOH}$ . The decreasing acidic character of some of the common acids in  $\text{CH}_3\text{COOH}$  has been found to be as follows:



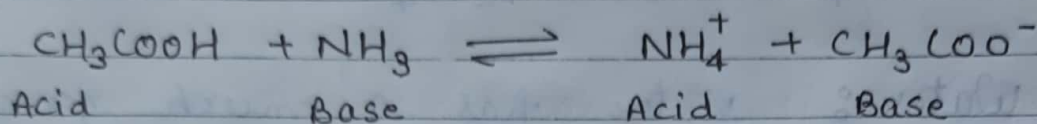
(ii) Water: Water has a much greater tendency to accept protons than  $\text{CH}_3\text{COOH}$ . The ionization of strong acid,  $\text{HCl}$  in this medium may be represented as:



The equilibrium shifts very much to the right. Thus, all the strong acids react almost completely with water to form  $\text{H}_3\text{O}^+$  ions. Therefore all strong acids in aqueous solution are almost equally strong. This phenomenon is known as **levelling effect**.

However, in the case of weak acids like  $\text{HCOOH}$ ,  $\text{CH}_3\text{COOH}$  etc, the equilibrium is not much shifted towards right. It is therefore possible to distinguish between their relative strengths.

(iii) Liquid ammonia: Liquid  $\text{NH}_3$  has a strong tendency to accept protons. In this medium even a weak acid, e.g.  $\text{CH}_3\text{COOH}$  ionizes to a considerable extent and, thus, behaves as a strong acid.



The equilibrium shifts very much to the right. Thus all the acids which in the aqueous solutions behave stronger than  $\text{CH}_3\text{COOH}$ , appear to be of about the same strength when dissolved in liquid  $\text{NH}_3$ .

(b) Base strength: The strength of a base also depends upon the nature of solvent. If the solvent is a weak acid such as water, the strength of different bases can be compared as they will ionize to different extent. If the solvent is slightly stronger acid, e.g.  $\text{CH}_3\text{COOH}$ , the strengths of different bases cannot be compared.

for Example:  $\text{NaOH}$  is a strong base and  $\text{NH}_4\text{OH}$  is a weak base in water but both are equally strong when  $\text{CH}_3\text{COOH}$  is used as a solvent. (levelling effect).



2. Effect of Polarity and dielectric constant on relative strength of acid and bases -:

The relative strength of acids and bases is also affected by the polarity and dielectric constant of the medium. Greater is the polarity and would be the acidic or basic strength of the species dissolved in that solvent.

3. Effect of Substituents on relative strength of acids and base -:

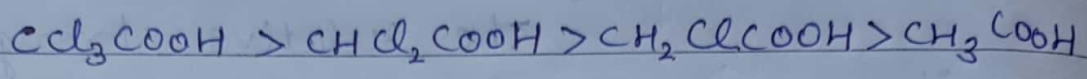
The relative of acids and bases is affected by the nature, number and type of bonding present in the substituents.

(a) Electron withdrawing (-I) or electron releasing (+I) nature of Substituents -:

Since the acid is an electron acceptor and the base is an electron donor, their acidic and basic strengths will be considerably affected by the nature of substituents.

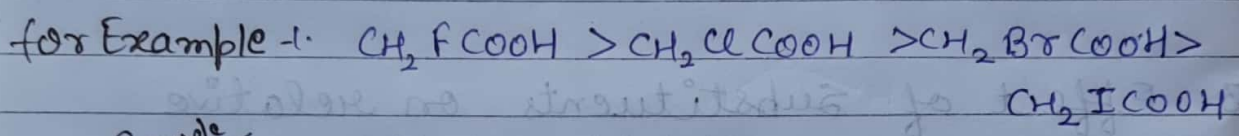
1. An electron withdrawing substituent will increase the acidic strength.

for Example - the acidic character of chloro acids is in the order.



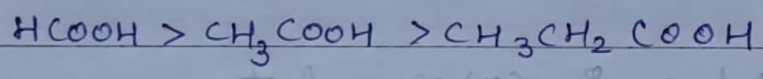
This is because Cl is an electron withdrawing substituent. (-I)

2. Greater is the electronegativity of halogen atom, greater is the acidic strength.



Example 2  
3. An electron releasing substituent will decrease the acidic strength.

for Example - The acidic character of alkyl acids is in the order:



This is because alkyl group is an electron releasing group. (+I)

Similarly, the electron withdrawing substituent will decrease the base strength whereas the electron releasing substituent will increase the base strength.

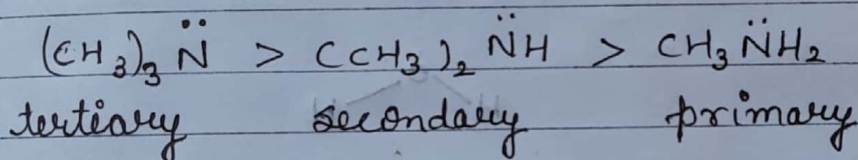
It is for this reason that  $C_6H_5NH_2$  is less basic than  $NH_3$  whereas  $CH_3NH_2$  is more basic than  $NH_3$ .

for Example -  $\text{CH}_3\text{NH}_2 > \text{NH}_3 > \text{C}_6\text{H}_5\text{NH}_2$

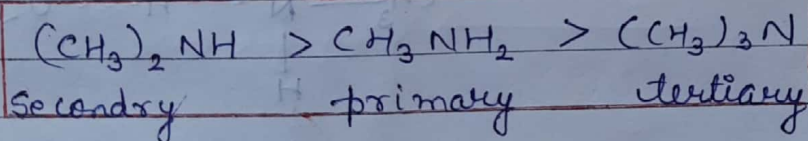
(b) Steric and solvation effects:

The steric and solvation effects also affect the relative strengths of bases.

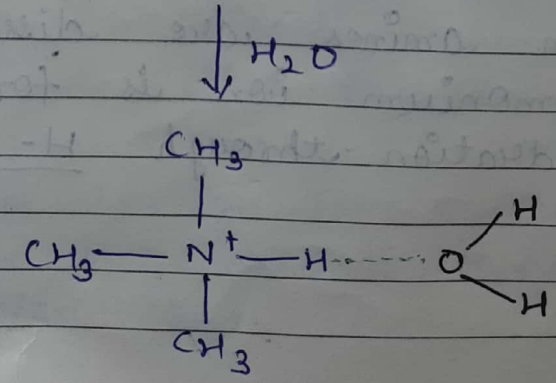
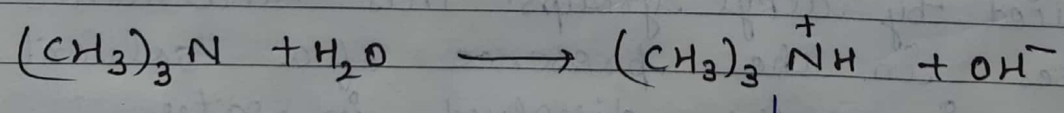
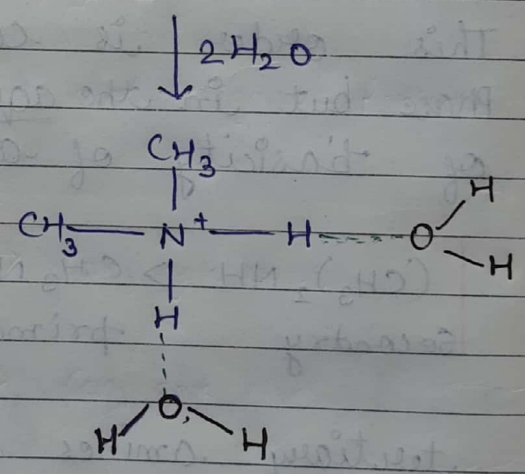
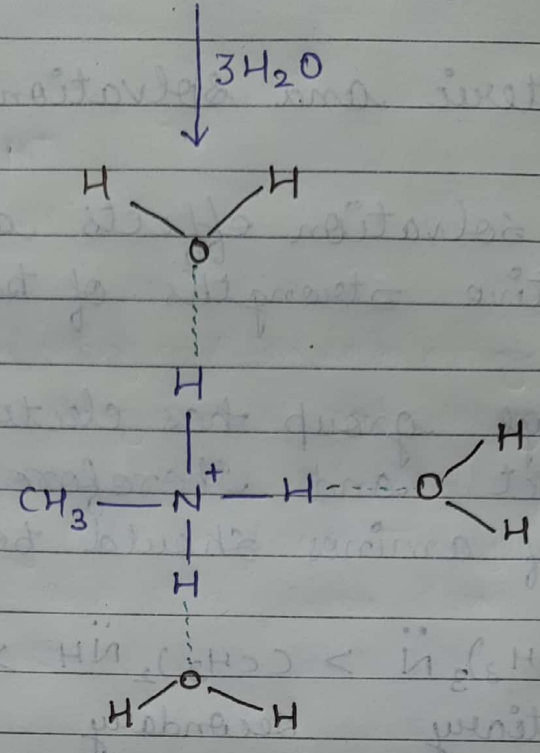
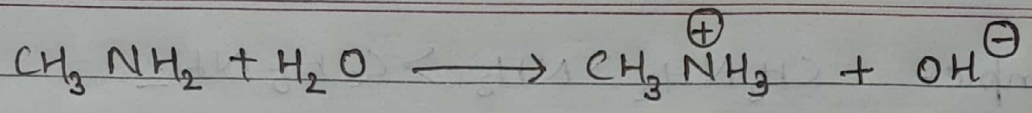
Alkyl group has electron releasing (+I) effect and therefore the basic strength of amines should be in the order:



★ This order is correct in the gas phase but in the aqueous solution the order of basicity of amines is:



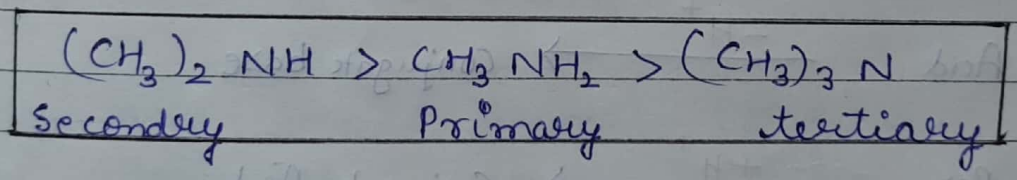
The tertiary amines are even less basic than primary amines due to steric hindrance produced by alkyl groups. This hindrance arises in the presence of a solvent. When amines are dissolved in water ammonium ion is formed which undergoes hydration through H-bonding.



The greater is the number of hydrogen bonds formed by the ammonium ion of base amine, the larger will be the heat of hydration and greater will be the stability.

These ammonium ions are obtained from primary, secondary and tertiary amines, respectively. This order of basic character of amines is reverse to that expected from inductive effect. Thus, the actual basic character of an amine is the combined effect of the inductive effect of substituent and solvation effect.

As a result of these two effects, the basic character of amines is in the order:



(c) Nature of bonding present in the substituents:

The presence of a  $\pi$ -bond in the substituent changes the acidic or basic character of the species.

# SUMMARY OF THE CHAPTER

## OR SOME IMPORTANT POINTS

According to Arrhenius-

Acid gives -  $H^+$

Base gives -  $OH^-$

NOTE - More  $K \rightarrow$  More strong acid or more strong base  
Less  $pK \rightarrow$  More strong acid or more strong base

Bronsted - Lowry Theory (Proton donor Theory)

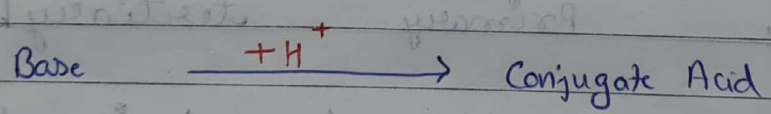
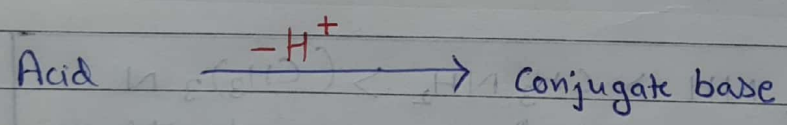
According to this theory Acid is a proton donor and Base is a proton acceptor.

For example -

$HCl$  is Acid Its conjugate base is  $Cl^-$

$NH_3$  is Base Its conjugate Acid is  $NH_4^+$

NOTE - Positive Radicals are Acid and Negative Radicals are base



Acid

Conjugate base

$HCl$

$Cl^-$

$HNO_3$

$NO_3^-$

$H_3PO_4$

$H_2PO_4^-$

$CH_3COOH$

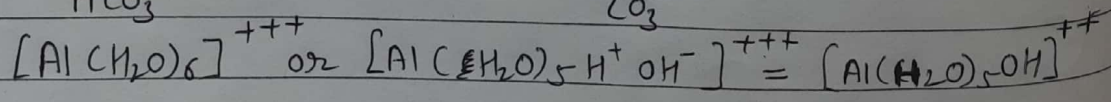
$CH_3COO^-$

$H_2O$

$OH^-$

$HCO_3^-$

$CO_3^{2-}$



### Amphoteric Substance -

Which are capable of donating as well as accepting the proton.

Example -  $H_2O$ ,  $NH_3$ ,  $HCO_3^-$ ,  $HSO_4^-$

NOTE → NaOH is base according to Arrhenius theory because it gives  $OH^-$  in aqueous solution but according to Bronsted theory it is not a base because it does not accept  $H^+$  (proton)

⇒ Conjugate base of strong acid is weak and vice versa  
for example -

Strong Acid	Ex - HCl	$Cl^-$ (weak base)
Weak Acid	Ex $CH_3COOH$	$CH_3COO^-$ (Strong base)

⇒ Arrhenius Acid are also Bronsted Acid Ex HCl  
Arrhenius Base are not Bronsted base Ex NaOH

### Lewis Concept of Acid & Bases -

1. Lewis Acid ( Lone Pair Acceptor) - (Electrophile)

Lewis Acid is Lone Pair of electron acceptor

Example -  $BF_3$ ,  $AlCl_3$ ,  $FeCl_3$ ,  $ZnCl_2$ ,  $Cu^{++}$ ,  $Ag^+$ ,  $Fe^{++}$ ,  $SO_3$

2.

2. Lewis Base - Lewis Base is lone Pair donor (Nucleophile)

Example -  $NH_3$ ,  $H_2O$ ,  $R-OH$ ,  $R-O-R$ ,  $RNH_2$ ,  $CN^-$

### LEWIS ACID

The following species can act as Lewis Acid -

- (1) Molecule in which central atom has incomplete octet
- (2) Simple Cation can act as Lewis Acid
- (3) Molecule In which central atom has empty d orbitals

Ex -  $\text{SiF}_4$ ,  $\text{PF}_5$ ,  $\text{AlCl}_3$ ,  $\text{BF}_3$ ,  $\text{PCl}_3$ ,  $\text{SnCl}_4$  etc.

(4) Molecules in which atoms of dissimilar electronegativities are joint by multiple bonds

Ex -  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_3$  etc.

**LEWIS BASE -**

The following species can act as Lewis base

- (1) Negatively charged ion
- (2) Neutral species having at least one lone pair of electrons

NOTE - All Bronsted bases are also Lewis base but all bronsted acids are not Lewis Acid

	Arrhenius	Bronsted	Lewis
Acid	$\text{H}^+$ donor	$\text{H}^+$ donor	Lone Pair Acceptor
Base	$\text{OH}^-$ donor	$\text{H}^+$ acceptor	Lone Pair donor