

Acids and Bases

Introduction

Throughout the history of chemistry, various acid-base concepts have been proposed and used. In this section, we shall briefly discuss the different concepts put forth from time to time. Each of these can be applied with advantage in appropriate circumstances. In a given situation, the chemist uses the concept that suits his purpose best.

I. Classical Concept (Operational Definitions)

The earliest classification of substances into acids and bases was based upon the characteristic properties possessed by each one of them. For example,

Acid was defined as a substance whose aqueous solution possessed the following characteristic properties:

(i) conducts electricity (ii) reacts with active metals like zinc, magnesium etc. to give hydrogen (iii) turns blue litmus red (iv) has a sour taste. (v) whose acidic properties disappear on reaction with a base.

Base was defined as a substance whose aqueous solution possessed the following characteristic properties:

(i) conducts electricity (ii) turns red litmus blue (iii) has a bitter taste (iv) has a soapy (slippery) touch (v) whose basic properties are destroyed on reaction with an acid.

The above definitions of acids and bases are called *operational definitions* as they are based upon certain operations (i.e., tests) to be performed on the substances. The above definitions of acids and bases have been replaced by *conceptual definitions* (put forward by Arrhenius, Bronsted-Lowry and Lewis) which go into the causes of the observed behaviour based upon structure and composition of the substances.

II. Arrhenius Concept: Water Ion Concept

To explain the observed properties of electrolytes, Arrhenius in 1884 put forward a theory, popularly known as '*Arrhenius theory of ionization*'. The main idea contained in this theory was that when an electrolyte is dissolved in water, it dissociates into positively and negatively charged ions.

Based upon this theory, Arrhenius gave the definitions of acids and bases as follows:

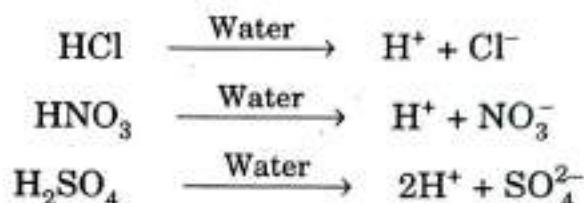
Acids

An acid is defined as a substance which contains hydrogen and which when dissolved into water gives hydrogen ions (H^+)

Arrhenius Classification of Acids

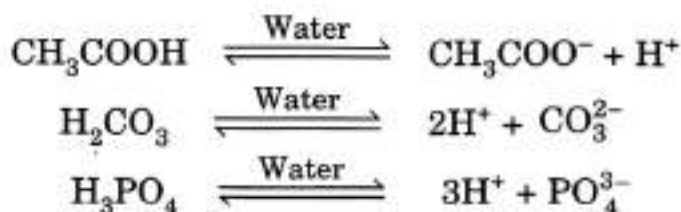
On the basis of Arrhenius definition of acids, acids have been classified as strong acids and weak acids.

1. Strong acids. Substances like HCl , HNO_3 and H_2SO_4 containing hydrogen, when dissolved in water dissociate completely into H^+ ions and the negative ions as follows:

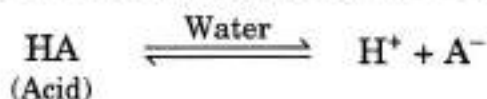


Such acids are called **strong acids**.

2. Weak acids. Substances like acetic acid (CH_3COOH), carbonic acid (H_2CO_3), phosphoric acid (H_3PO_4), etc., when dissolved in water dissociate into ions to a small extent. Thus, an equilibrium is set up between the ions and the undissociated molecules as follows:



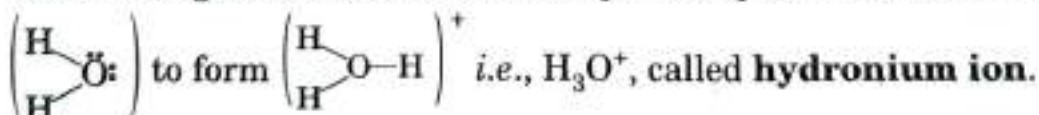
Such acids are called **weak acids**. In general, we can write



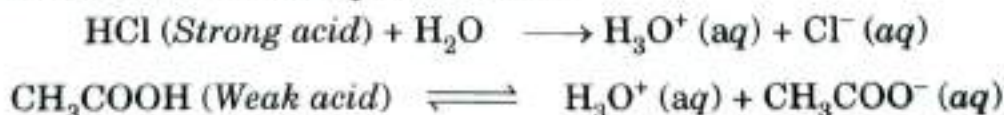
In fact, all the properties of an acid are due to the H^+ ions which it furnishes in aqueous solution.

Formation of hydronium ion (H_3O^+) in aqueous solution

H^+ ion is simply a proton which is very small in size (radius $\sim 10^{-13}$ cm). It has a strong electric field. It takes up a lone pair of electrons from water molecule



Hence we simply represent H^+ ion as $H_3O^+(aq)$. Thus the dissociation of an acid in aqueous solution can be represented as:



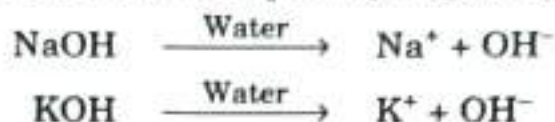
Bases

A base is defined as a substance which contains hydroxyl groups and which when dissolved in water gives hydroxide ions (OH^-)

Classification of Arrhenius Bases

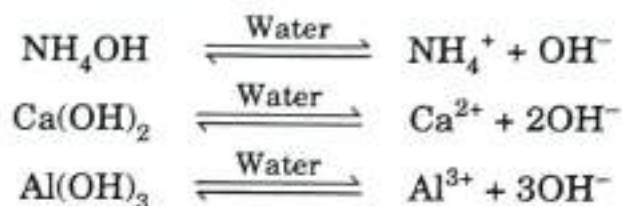
On the basis of Arrhenius definition of bases, bases have been classified as strong bases and weak bases.

1. Strong bases. Substances like NaOH and KOH containing the $-OH$ groups, when dissolved into water, dissociate **completely** to give OH^- ions as follows:



These are called **strong bases**.

(ii) **Weak bases.** Substances like NH_4OH , $Ca(OH)_2$, $Mg(OH)_2$, $Al(OH)_3$, etc. dissociate to a small extent as follows:



These are called **weak bases**.

In aqueous solution OH^- ion is generally represented as $OH^-(aq)$. Hence the dissociation of bases in aqueous solution may be represented as:

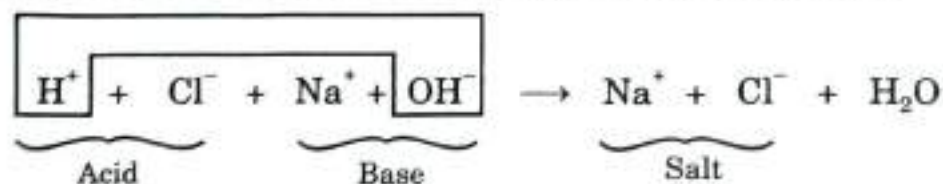


Neutralisation Reaction According to Arrhenius Concept

According to Arrhenius concept of acids and bases, neutralisation reaction is a process in which an acid and a base react together to form salt and H_2O .



Actually this reaction takes place through the following steps:



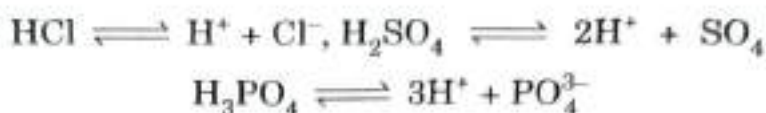
or



Thus neutralisation is a process in which H^+ and OH^- ions combine together and form unionised molecules of water (H_2O). As a result of this process, the characteristic properties of acids and bases are destroyed.

Basicity or Protocity of an Arrhenius Acid.

The number of H^+ (or H_3O^+) ions given by one molecule of an Arrhenius acid is known as the basicity or protocity of the acid. For example the basicity of HCl , H_2SO_4 and H_3PO_4 is one, two and three respectively as shown below:

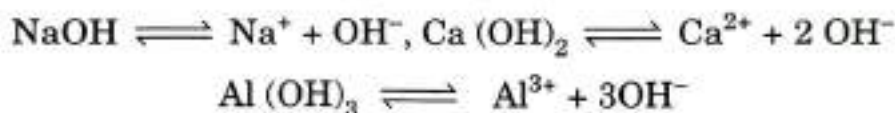


Monobasic (Monoprotonic) and Polybasic (Polyprotonic) Acids

The acids giving one, two and three H^+ ions in aqueous solution are called *monobasic (monoprotonic) acids* (e.g. HCl , HF , HNO_3 , CH_3COOH etc.), *dibasic (diprotonic) acids* [e.g. H_2SO_4 , H_2CO_3 , H_2S , $(\text{COOH})_2$ etc.] and *tribasic (triprotonic) acids* (e.g. H_3PO_4 etc.). Dibasic and tribasic acids are called *polybasic or polyprotonic acids*.

Acidity or Hydroxity of an Arrhenius Base.

The number of OH^- ions given by one molecule of an Arrhenius base is known as the *acidity or hydroxity of the base*. For example the acidity of NaOH , $\text{Ca}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ is one, two and three respectively as shown below:



Monoacidic (Monohydroxic) and Polyacidic (Polyhydroxic) Bases

The bases giving one, two and three OH^- ions in aqueous solution are called *monoacidic (monohydroxic) bases* (e.g. NaOH , NH_4OH etc), *diacidic (dihydroxic) bases* [e.g. $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$ etc] and *triacidic (trihydroxic) acids* [e.g. $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$ etc]. Diacidic and triacidic bases are called *polyacidic or polyhydroxic bases*.

Relative Strength of Acids and Bases According to Arrhenius Concept

According to Arrhenius concept, greater is the number of H^+ ions produced by an acid in aqueous solution, stronger is the acid. Similarly greater is the number of OH^- ions produced by a base in aqueous solution, stronger is the base.

We know that greater is the value of acid dissociation constant of an acid (K_a), greater is the amount of H^+ ions produced by the dissociation of the acid in aqueous solution and hence stronger is the acid. Thus greater is the value of K_a of an acid, greater is the strength of weak acids. Similarly greater in the value of base dissociation constant of a base (K_b), greater is the amount of OH^- produced by the dissociation of the base in aqueous solution, greater is the strength of the weak bases.

Utility of Arrhenius Concept

(i) Since the reaction representing neutralisation process involves the combination H^+ and OH^- ions, the approximately constant molar heat of neutralisation would be expected. Thus the constant heat of neutralisation of a strong acid by a strong base is readily understandable in terms of this concept.

(ii) This concept has offered a means of correlating catalytic behaviour with the concentration of the H^+ ion.

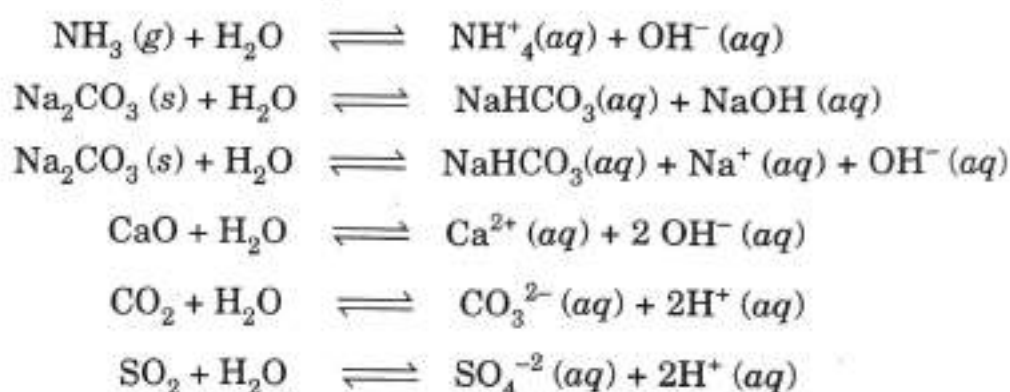
(iii) The Arrhenius concept of acids and bases is able to explain a number of phenomena like neutralization, salt hydrolysis, strength of acids and bases etc.

Limitations of Arrhenius Concept

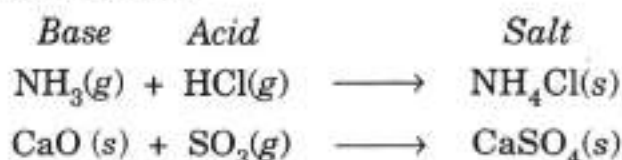
(i) *Nature of H^+ ions and OH^- ions:* According to Arrhenius concept, acids and bases were defined as substances which gave H^+ ions and OH^- ions respectively in aqueous solution. But as discussed above, these ions cannot exist as such in the aqueous solution but exist as hydrated ions, written as $H^+(aq)$ and $OH^-(aq)$.

(ii) *Inability to explain acidic and basic character of certain substances:* Arrhenius concept demands that an acid must contain hydrogen and a base must contain hydroxyl (OH^-) groups. However, a number of substances like NH_3 , Na_2CO_3 , CaO etc., are known to be basic but do not contain any hydroxyl groups. Similarly, a number of substances like CO_2 , SO_2 , SO_3 etc., are known to be acidic but do not contain any hydrogen.

This limitation is, however, overcome if water is supposed to play an important role. This is clear from the following reactions:



(iii) *Inability to explain the reaction between an acid and base in absence of water:* Two important examples are:



(iv) According to this concept, HCl is regarded as an acid only when dissolved in H_2O and not in some other solvent such as C_6H_6 or when it exists in the gaseous form.

(v) It cannot account for the acidic and basic character of the materials in non-aqueous solvents, e.g., NH_4NO_3 in liq. NH_3 acts as an acid, though it does not give H^+ ions. Similarly many organic materials and NH_3 , which do not have OH^- ions at all, are actually known to show basic character.

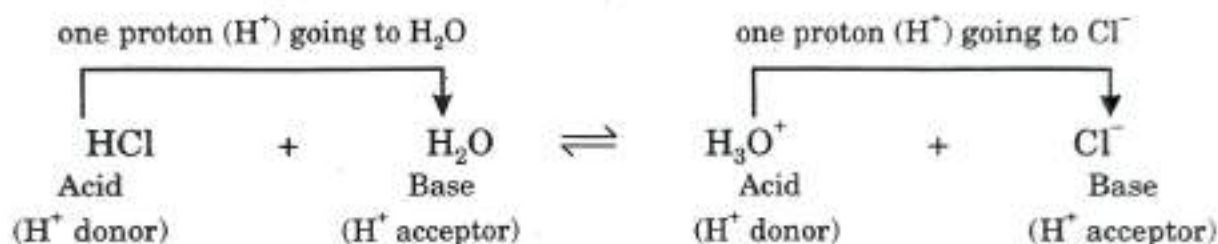
(vi) The neutralisation process is limited to those reactions which can occur in aqueous solutions only, although reactions involving salt formation do occur in many other solvents and even in the absence of solvents.

(vii) It cannot explain the acidic character of certain salts such as $AlCl_3$ in aqueous solution.

III. Bronsted-Lowry Concept: Proton Donor-Acceptor Concept

Definition – To overcome the limitations of Arrhenius concept, Bronsted (a Danish chemist) and Lowry (an English chemist) independently and simultaneously, in the year 1923, proposed a broader concept of acids and bases.

According to this concept, an acid is defined as any hydrogen containing material (a molecule or a cation or an anion) that can release a proton (H^+) to any other substance, whereas a base is any substance (a molecule or a cation or an anion) that can accept a proton from any other substance. In short, *an acid is a proton-donor and a base is a proton-acceptor*. As an example consider the reaction between HCl and H_2O as given below:



In this reaction HCl donates a proton to H_2O and is, therefore, an acid. Water, on the other hand, accepts a proton from HCl, and is, therefore, a base. In the reverse reaction which at equilibrium proceeds at the same rate as the forward reaction, H_3O^+ ion donates a proton to Cl^- ion and hence H_3O^+ ion is an acid. Cl^- ion, because it accepts a proton from H_3O^+ ion, is a base.

Points to Be Noted

(i) A substance acts as a Bronsted acid, *i.e.* gives a proton only when another substance to accept the proton (*i.e.* base), donated by the acid is also present. For example CH_3COOH does not act as an acid in C_6H_6 solution because the latter does not accept the proton donated by CH_3COOH .

(ii) According Bronsted-Lowry concept the presence of hydroxyl groups (OH^-) is not essential for a substance to act as a base. The only requirement is that the substance should have tendency to accept a proton.

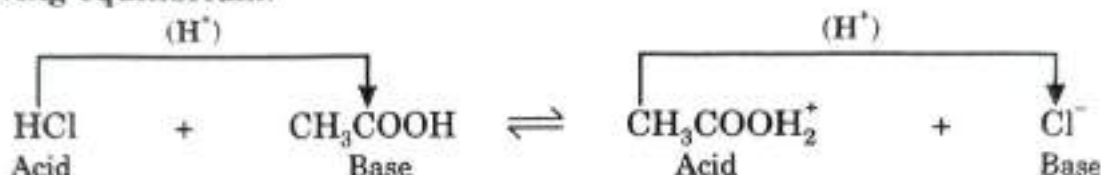
Examples of Bronsted-Lowry Acids and Bases

As already stated, Bronsted-Lowry acids and bases may be molecular, cationic and anionic species. Examples of such species are given below:

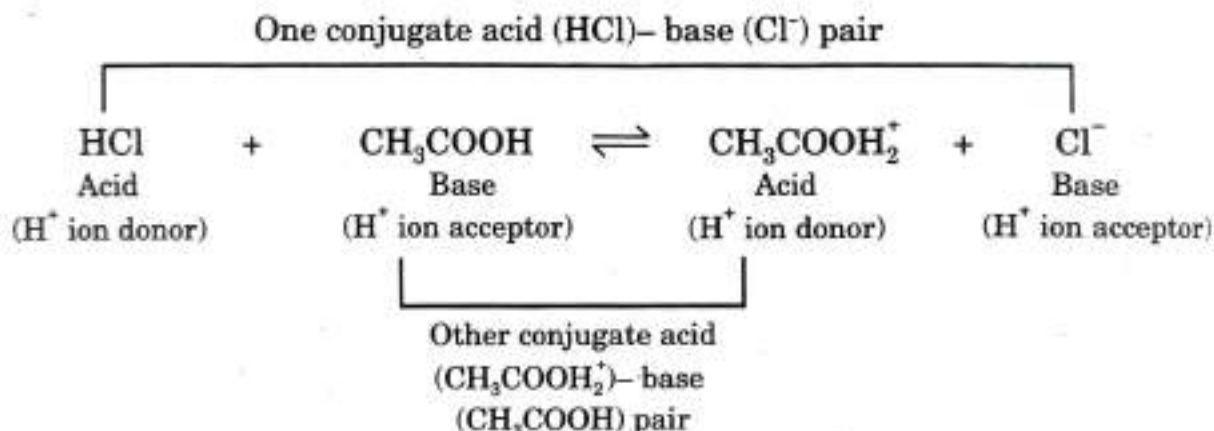
Type of Species	Acids	Bases
Molecular	HCl, HBr, $HClO_4$, HNO_3 , H_2SO_4 , H_3PO_4 , H_2O	NH_3 , N_2H_4 , amines, H_2O , NH_2OH
Cationic	NH_4^+ , $[Fe(H_2O)_6]^{3+}$, $[Al(H_2O)_6]^{3+}$, H_3O^+ ,	$[Fe(H_2O)_5(OH)]^{2+}$, $[Al(H_2O)_5(OH)]^{2+}$
Anionic	HCO_3^- , HSO_4^-	Cl^- , Br^- , I^- , OH^- , CO_3^{2-} , SO_4^{2-} , H^- , NH_2^- , OH^- , HS^-

Conjugate Acid-Base Pairs

In order to understand the concept of conjugate acid-base pair let us consider the following equilibrium.



If we consider the forward reaction of this equilibrium, we find that since HCl donates a proton (H^+) to CH_3COOH , HCl acts as a Bronsted acid. Since CH_3COOH accepts a proton from HCl, CH_3COOH acts as a Bronsted base. If we consider the reverse reaction of this equilibrium, we find that since $\text{CH}_3\text{COOH}_2^+$ donates a proton to Cl^- ion, $\text{CH}_3\text{COOH}_2^+$ acts as a Bronsted acid. Since Cl^- ion accepts a proton donated by $\text{CH}_3\text{COOH}_2^+$, it acts as a Bronsted base. In the given equilibrium the two acid-base pairs namely HCl (acid)– Cl^- (base) and $\text{CH}_3\text{COOH}_2^+$ (acid)– CH_3COOH (base) are called conjugate acid-base pairs.



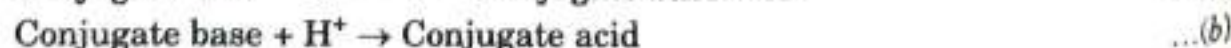
From the above acid-base equilibrium the following points may be noted:

(i) There is one acid and one base on each side of the equilibrium. If HCl (acid) is designated as Acid_1 or A_1 , then its conjugate base *viz* Cl^- ion may be designated as Base_1 or B_1 . Similarly CH_3COOH (base) is designated as Base_2 or B_2 and its conjugate acid *viz* $\text{CH}_3\text{COOH}_2^+$ is designated as Acid_2 or A_2 . Thus the above equilibrium can also be written as:

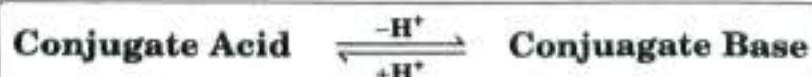


(ii) Each acid-base reaction has two conjugate acid-base pairs.

(iii) Conjugate base of a given acid is obtained by eliminating (removing) a proton from the acid. Similarly, a conjugate acid of a given base is obtained by adding a proton to the base. Thus:



Above two relations *viz* (a) and (b) can be combined to get:

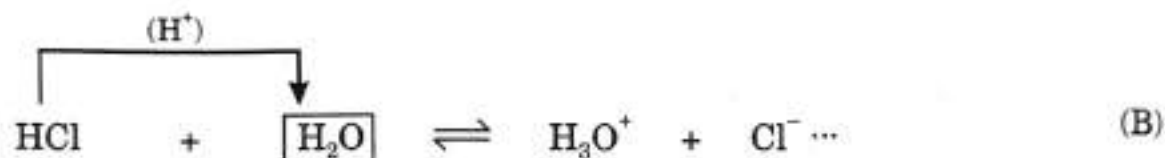
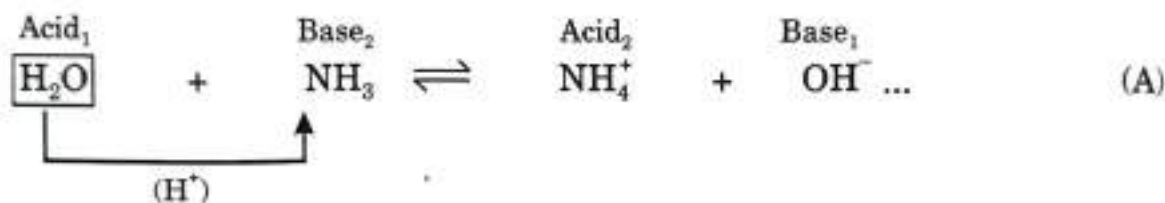


Thus we see that HA (acid) – A⁻(base) and BH⁺ (acid) – B (base) are two conjugate acid-base pairs in the above acid-base neutralisation reaction.

Amphiprotic Substances

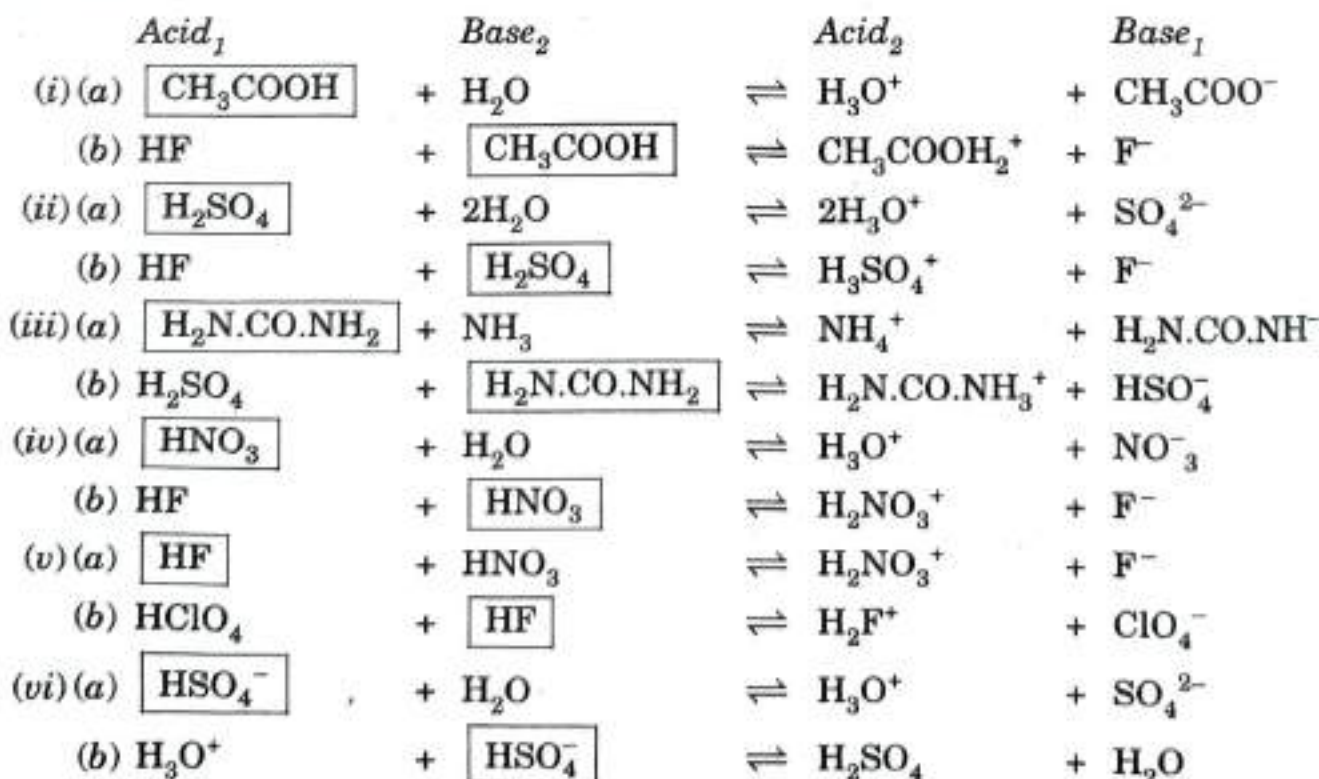
Molecules or ions that can lose as well accept proton(s) are called amphiprotic substances, *i.e.*, the molecules or ions that can act as Bronsted acids (loss of proton) as well as Bronsted bases (gain of proton) are called amphiprotic substances.

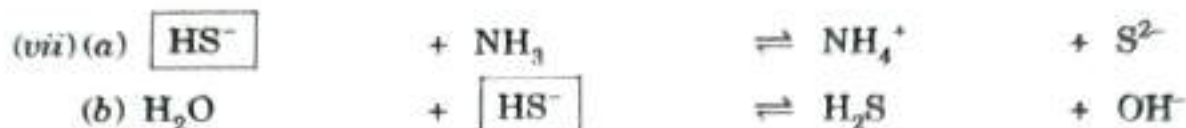
Illustration. As an example, let us consider the behaviour of H₂O in the following acid-base reactions:



In reaction (A) H₂O molecule loses a proton (H₂O $\xrightarrow{-\text{H}^+}$ OH⁻) and hence acts as an acid while in reaction (B) this molecule gains a proton from HCl (H₂O $\xrightarrow{+\text{H}^+}$ H₃O⁺) and hence behaves as a base. Thus since H₂O can lose as well as gain a proton, it behaves as an acid as well as a base. In other words, we say that H₂O is an amphiprotic substance.

Examples of other species (molecules or ions) which act as amphiprotic substances are given in the following acid-base reactions. Amphiprotic substances have been shown in a box.

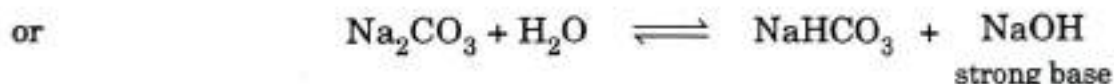
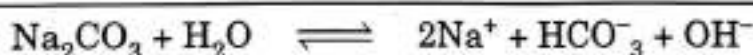
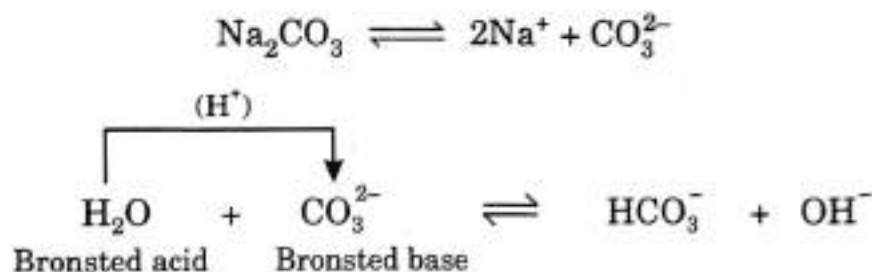




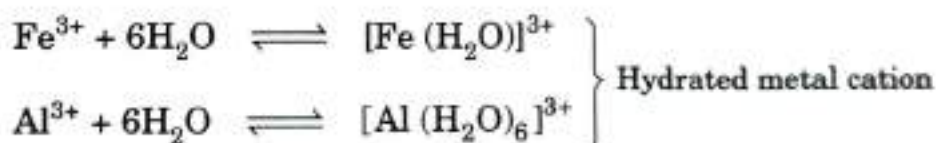
Applications of the Dual Behaviour of Water (H₂O)

Acid-base reactions (A) and (B) given above show that since H₂O acts both as Bronsted acid [i.e. proton donor] as shown in reaction (A)] and as Bronsted base [i.e. proton acceptor as shown in reaction (B)], H₂O shows dual behaviour. The dual behaviour of H₂O has been used to explain the following.

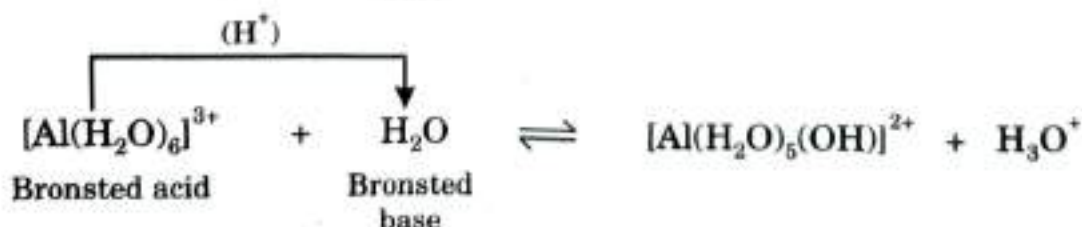
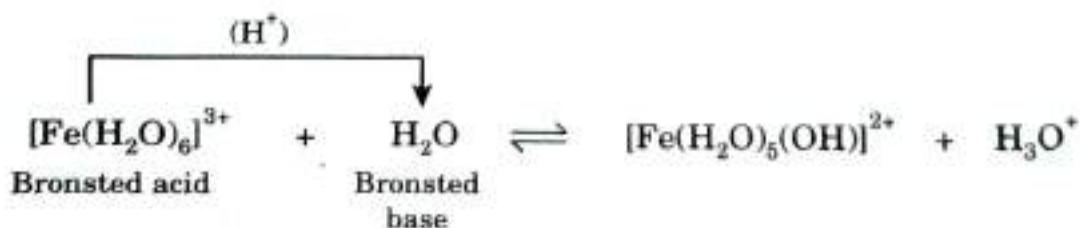
(i) **Aqueous solution of Na₂CO₃ is alkaline.** When Na₂CO₃ is dissolved in H₂O, CO₃²⁻ ions are obtained. Since CO₃²⁻ ion is a strong proton-acceptor, it accepts a proton from H₂O to produce HCO₃⁻ and OH⁻ ions. Finally NaHCO₃ and NaOH are produced. Since NaOH is a strong base, the aqueous solution of Na₂CO₃ shows alkaline nature.



(ii) **Aqueous solutions of the salts of Fe³⁺, Al³⁺ etc., are acidic.** Aqueous solutions of the salts of Fe³⁺, Al³⁺ etc. get hydrated to form hydrated metal cations, e.g.



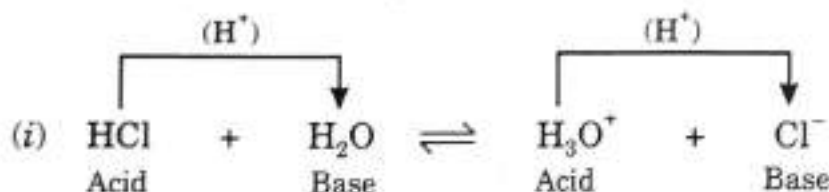
The hydrated metal cations are strong proton donors and hence donate a proton to H₂O to produce H₃O⁺ ions which make the solution acidic



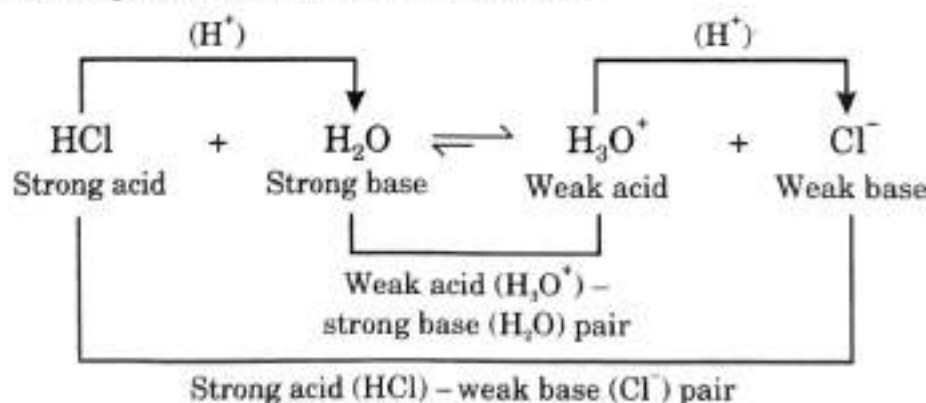
It may be noted from the above examples that in example (i) H_2O acts as a Bronsted acid while in example (ii), H_2O acts as a Bronsted base. Thus H_2O shows dual behavior.

In a Conjugate Acid-Base Pair Strong Acid has its Weak Conjugate Base and Vice Versa

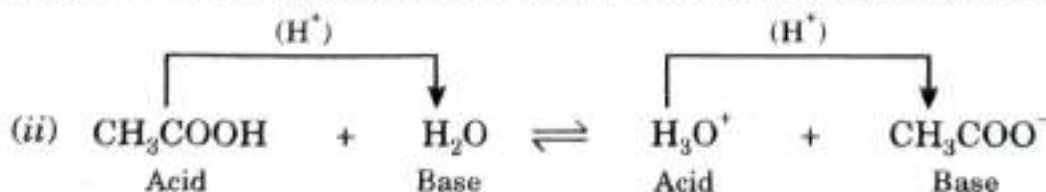
We know that according to Bronsted-Lowry concept, an acid-base reaction has two conjugate acid-base pairs. Each of the two conjugate acid-base pairs is a *strong acid-weak base pair* or a *weak acid-strong base pair*. Thus in a conjugate acid-base pair a strong acid has its weak conjugate base and vice versa. This fact can be proved by considering the following two acid-base equilibria.



In this reaction HCl and H_3O^+ are two acids and H_2O and Cl^- are two bases. Suppose this reaction proceeds from left to right. Hence HCl (acid) has stronger tendency to donate a proton (H^+) to H_2O (base) than H_3O^+ (acid) which donates a proton to Cl^- ion (base). Thus HCl is a stronger acid than H_3O^+ . In other words we can say that *HCl is a strong acid and H_3O^+ is a weak acid*. Further, since the reaction proceeds from left to right, H_2O (base) has stronger tendency to accept a proton from HCl (and) than Cl^- ion (base) which accepts a proton from H_3O^+ (acid). Thus H_2O is a stronger base than Cl^- ion. In other words we can say that *H_2O is a strong base and Cl^- ion is a weak base*. Above discussion shows that the acid-base reaction given above can be written as:

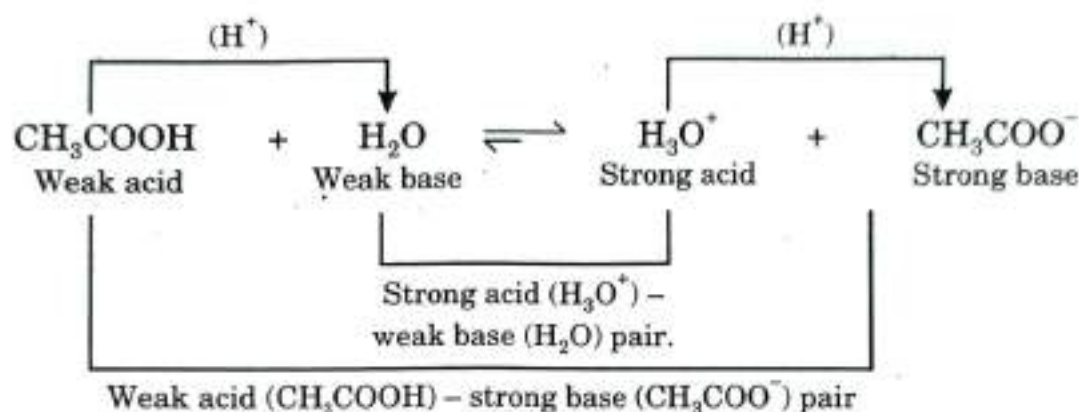


In this reaction the longer half arrow (\longrightarrow) indicates the direction of the reaction. It may be seen that if an acid-base reaction proceeds from left to right, the reacting acid and base both are strong and the acid and base produced both are weak.



In reaction (ii), CH_3COOH and H_3O^+ are two acids, and H_2O and CH_3COO^- are two bases. Suppose this reaction proceeds from right to left. Hence H_3O^+ (acid) has

stronger tendency to donate a proton to CH_3COO^- (base) than CH_3COOH (acid) which donates a proton to H_2O (base). Thus H_3O^+ is a strong acid and CH_3COOH is a weak acid. Further, since the reaction proceeds from right to left, CH_3COO^- (base) has stronger tendency to accept a proton from H_3O^+ (acid) than H_2O (base) which accepts a proton from CH_3COOH (acid). Thus CH_3COO^- is a strong base and H_2O is a weak base. Above discussion shows that the acid-base reaction (ii) can be written as:



In the above reaction, the longer half arrow (\longleftarrow) indicates the direction of the acid-base reaction. It may be seen that if an acid-base reaction proceeds from right to left, the reacting acid and base both are weak and the acid and base produced both are strong.

Above discussion shows that *in a conjugate acid-base pair in an acid-base reaction, if the acid is strong, the conjugate base of this acid would be weak and vice versa*. In other words we can say that *an acid-base reaction has one strong acid-weak base pair and one weak acid-strong base pair*.

Relative Order of Basic Strength of Conjugate Bases of Given Conjugate Acids

We have seen that in a conjugate acid-base pair, if the acid is strong, its conjugate base would be weak. Similarly, if the acid is weak, its conjugate base would be strong.

Illustrative example Conjugate bases of HF, HCl, HBr and HI are F^- , Cl^- , Br^- and I^- respectively. We know that acidic strength of HF, HCl, HBr and HI in aqueous solution *increases* as $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$. This order shows that HF is the weakest acid and HI is the strongest acid. On the basis of the above rule, the conjugate base of the weakest acid, HF (i.e. F^- ion) would be the strongest base and the conjugate base of the strongest acid, HI (i.e. I^- ion) would be the weakest base. Thus the basic strength of the conjugate bases (i.e. F^- , Cl^- , Br^- and I^-) would be in the decreasing order $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$. It may be noted that the relative order of basic strength of bases (F^- , Cl^- , Br^- and I^-) is *opposite to relative order of acidic strength of acids (HF, HCl, HBr and HI)*

In Table 3.1, since the acid strength of the acids given in 1st column **decreases** from HClO_4 to CH_4 , the basic strength of the conjugate bases (given in 2nd column) of the acids **increases** from ClO_4^- (conjugate base of HClO_4) to CH_3^- (conjugate base of CH_4)

Table 3.1 Relative order of acid strength of acids and relative order of base strength of their conjugate bases.

Acid		Conjugate Base
HClO ₄ (Per chloric acid)		ClO ₄ ⁻ (Perchlorate ion)
H ₂ SO ₄ (Sulphuric acid)		HSO ₄ ⁻ (Hydrogen sulphate ion)
HI (Hydriodic acid)		I ⁻ (Iodide ion)
HBr (Hydrobromic acid)		Br ⁻ (Bromide ion)
HCl (Hydrochloric acid)		Cl ⁻ (Chloride ion)
HNO ₃ (Nitric acid)		NO ₃ ⁻ (Nitrate ion)
H ₃ O ⁺ (Hydronium ion)		H ₂ O (Water)
CCl ₃ COOH (Trichloroacetic acid)	Decreasing acid strength	CCl ₃ COO ⁻ (Trichloroacetate ion)
HSO ₄ ⁻ (Hydrogen sulphate ion)		SO ₄ ²⁻ (Sulphate ion)
H ₃ PO ₄ (Phosphoric acid)		H ₂ PO ₄ ⁻ (Dihydrogen phosphate ion)
HNO ₂ (Nitrous acid)		NO ₂ ⁻ (Nitrite ion)
HF (Hydrofluoric acid)		F ⁻ (Fluoride ion)
HCOOH (Formic acid)		HCOO ⁻ (Formate ion)
CH ₃ COOH (Acetic acid)		CH ₃ COO ⁻ (Acetate ion)
H ₂ CO ₃ (Carbonic acid)		HCO ₃ ⁻ (Hydrogen carbonate ion)
H ₂ S (Hydrogen sulphide)		HS ⁻ (Hydrogen sulphide ion)
NH ₄ ⁺ (Ammonium ion)		NH ₃ (Ammonia)
HCN (Hydrogen cyanide)		CN ⁻ (Cyanide ion)
C ₆ H ₅ OH (Phenol)		C ₆ H ₅ O ⁻ (Phenoxide ion)
HS ⁻ (Hydrogen sulphide ion)		S ²⁻ (Sulphide ion)
H ₂ O (Water)		OH ⁻ (Hydroxide ion)
C ₂ H ₅ OH (Ethanol)		C ₂ H ₅ O ⁻ (Ethoxide ion)
NH ₃ (Ammonia)		NH ₂ ⁻ (Amide ion)
H ₂ (Hydrogen)	H ⁻ (Hydride ion)	
CH ₄ (Methane)	CH ₃ ⁻ (Methide ion)	

Increasing base strength

Relative Strength of Acids and Bases According to Bronsted-Lowry Concept

According to Bronsted-Lowry concept, the relative strength of two acids (acid strength) is compared by comparing their tendency to donate proton (H⁺). Similarly the relative strength of two bases (base strength) is compared by comparing their tendency to accept proton. This discussion shows that the acids which can donate a proton (H⁺) to a base comparatively more easily or readily are said to be strong acids while the acids which donate a proton with great difficulty are said to be weak acids.

Similarly the bases that can accept a proton quite easily are said to be strong bases while the bases that can accept a proton with great difficulty are said to be weak bases.

Some Concepts

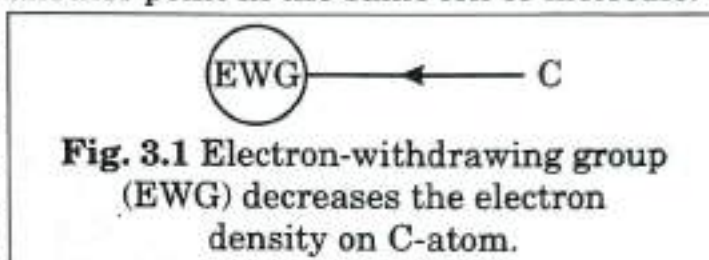
1. Electron-Withdrawing Groups (EWGs) and Electron-Donating Groups (EDGs)

EWGs are those which decrease the electron density and EDGs are those which increase the electron density. Examples of EWGs are $-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$, $-\text{X}$ (halogen), $-\text{OH}$, $-\text{C}_6\text{H}_5$ etc. and examples of EDGs are $-\text{R}$ (alkyl), $-\text{NH}_2$, $-\text{OR}$, $-\text{OCH}_3$, $-\text{COO}^-$ etc. EWG is also called **electron attracting group** and EDG is also called **electron repelling group** or **electron releasing group**.

2. Inductive Effect

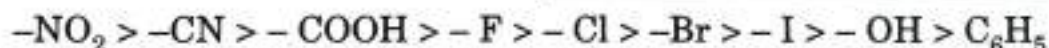
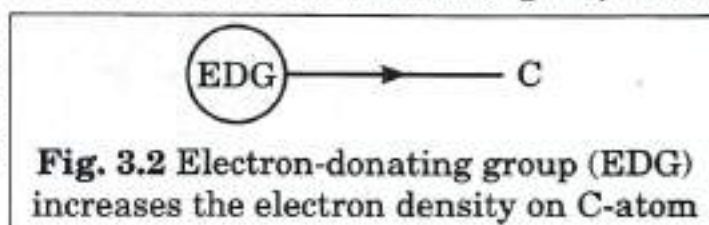
Inductive effect may be defined as the effect transferred by a charged atom at one point in an ion or a molecule to another point in the same ion or molecule.

Inductive effect caused by electron-withdrawing groups (EWG) (EWG is also called *electron attracting group*) decreases the electron density (*i.e.* disperses the negative charge) on the C-atom with which EWG is attached



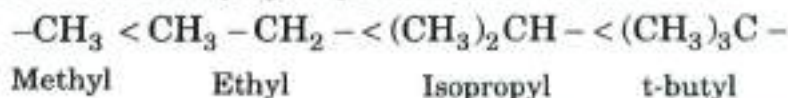
(See Fig. 3.1) and hence is called electron-withdrawing inductive effect. This effect is expressed as $-I$ effect. $-$ sign indicates that EWG decreases the electron density. $-I$ effect increases the acidic strength of acids and decreases the basic strength of bases.

Examples of species which have electron-withdrawing inductive effect ($-I$ effect) are $-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$, $-\text{X}$ (halogen), $-\text{OH}$, $-\text{C}_6\text{H}_5$ etc. $-I$ effect of these groups decreases in the order:



Inductive effect caused by electron-donating groups (EDG) (EDG is also called *electron repelling or electron releasing group*) increases the electron density (*i.e.* intensifies the negative charge) on C-atom with which EDG is attached (See Fig. 3.2) and hence is called electron-donating inductive effect. This effect is represented as $+I$ effect. $+$ sign indicates that EDG increases the electron density. $+I$ effect decreases the acid strength of acids and increases the basic strength of bases.

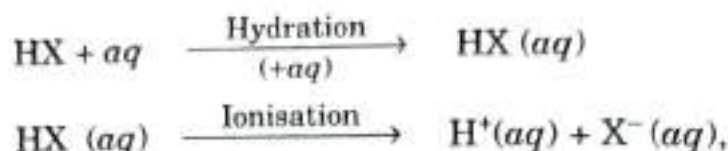
Examples of species which have electron-donating inductive effect ($+I$ effect) are $-\text{NH}_2$, $-\text{OR}$ (alkoxy group), $-\text{R}$ (alkyl group), $-\text{OCH}_3$ (methoxy group), $-\text{COO}^-$ etc. $+I$ effect of some alkyl groups increases in the order:



In general, $+I$ effect of alkyl groups is in the order: $1^\circ < 2^\circ < 3^\circ$.

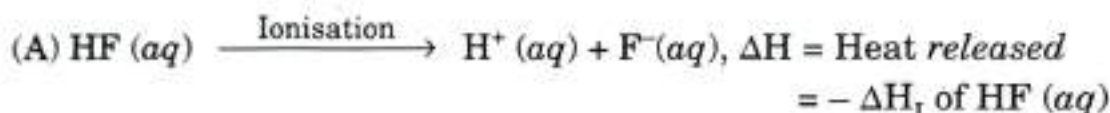
3. Heat of Ionisation (ΔH_i) of MX Molecules in Aqueous Solution

Heat of ionisation (ΔH_i) of HX molecule in aqueous solution is the amount of heat released ($-$ sign) when HX molecule undergoes ionisation to give H^+ and X^- ions in aqueous solution. Thus:



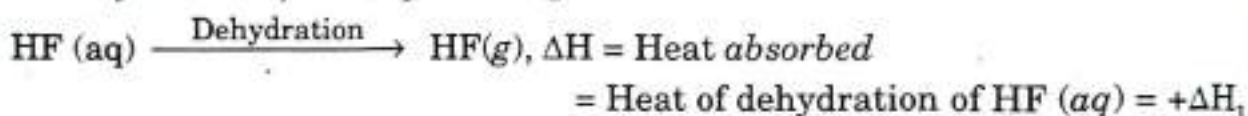
$\Delta H = \text{Heat released} = \text{Heat of ionisation of HX} (aq) = -\Delta H_1 \text{ of HX} (aq)$

Calculation of ΔH_1 for HX (aq) molecules As an example let us calculate the value of ΔH_1 for HF (aq) molecule. We know that HF, in aqueous solution, ionises to give $\text{H}^+(aq)$ and $\text{F}^-(aq)$ ions as shown below.

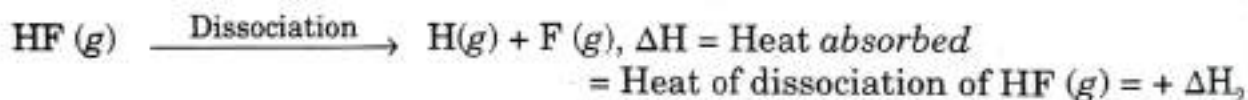


As a matter of fact, the ionisation reaction shown above takes place through the following steps:

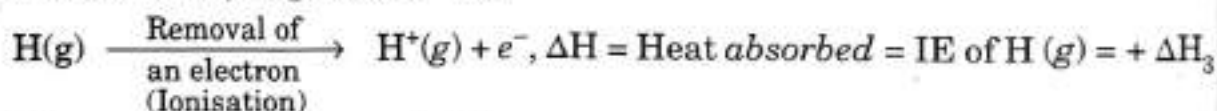
(a) Dehydration of HF (aq) to HF (g)



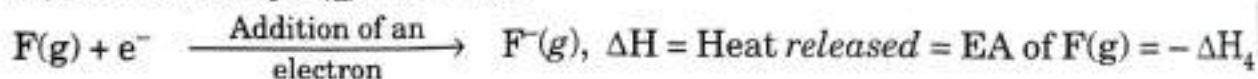
(b) Dissociation of HF (g) into H (g) and F (g)



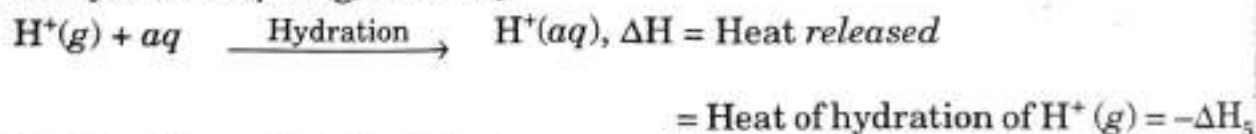
(c) Conversion of H(g) into H^+ (g)



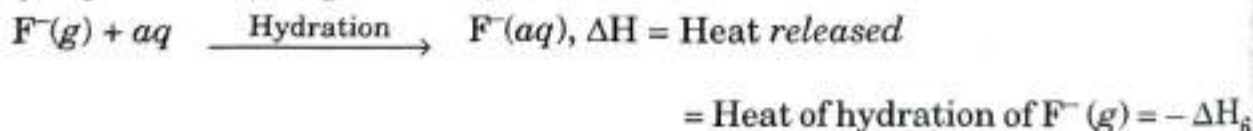
(d) Conversion of F(g) into F^- (g)



(e) Hydration of H^+ (g) to H^+ (aq)



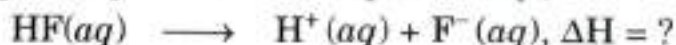
(f) Hydration of F^- (g) to F^- (aq)



On adding the equations given at (a), (b), (c), (d), (e) and (f), we get:



or



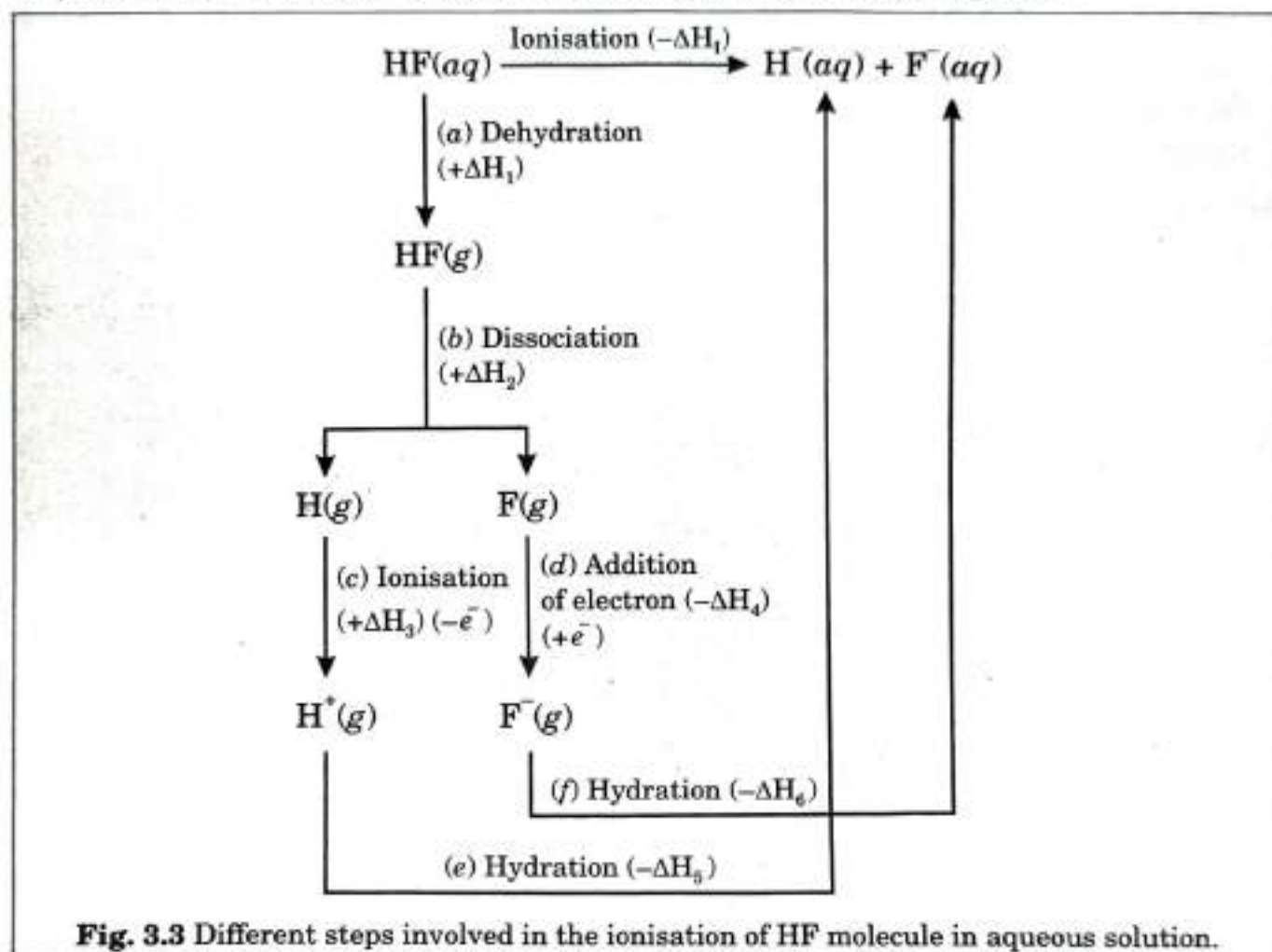
Since the above equation is the same as equation (A), ΔH for the above reaction is ΔH_1 , i.e. ΔH_1 is equal to the sum of ΔH for reactions (a), (b), (c), (d), (e) and (f). Thus:

$$\begin{aligned} \Delta H_1 \text{ for HF} (aq) &= \Delta H_1 + \Delta H_2 + \Delta H_3 + (-\Delta H_4) + (-\Delta H_5) + (-\Delta H_6) = \Delta H_1 + \Delta H_2 + \\ &\quad \Delta H_3 - \Delta H_4 - \Delta H_5 - \Delta H_6 \dots (i) \end{aligned}$$

If the values of ΔH_1 , ΔH_2 , ΔH_3 , ΔH_4 , ΔH_5 and ΔH_6 for HF molecule are put in equation (i), we get the value of ΔH_1 for HF molecule which is equal to

-12 kJ mol^{-1} . Similarly putting the values of ΔH_1 , ΔH_2 , ΔH_3 , ΔH_4 , ΔH_5 and ΔH_6 for HCl, HBr and HI molecules in equation (i), the values of ΔH_1 for these molecules have been found equal to -59 , -63 and -57 kJ mol^{-1} .

All the steps shown at (a), (b), (c), (d), (e), and (f) can be shown in a collective way in the form of a cycle known as Born-Haber cycle (See Fig. 3.3).

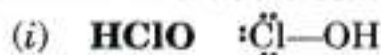


4. To Calculate the Formal Charge (m) of the Central Atom in Some Oxoacids.

Formal charge (m) of the central atom of an oxoacid is given by:

$m = \text{No. of electrons present in the valence shell of the central atom} - \text{No. of unused electrons on the central atom} - \frac{1}{2} \times \text{No. of electrons used in forming } \sigma\text{-bonds between the central atom and O-atoms.}$

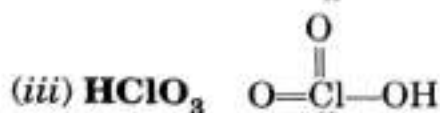
The value of m for some oxoacids has been calculated as follows;



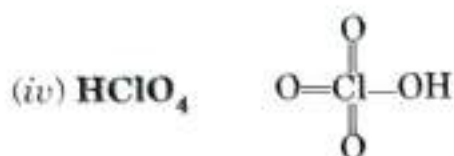
$$m = 7 - 6 - \frac{1}{2} \times 2 = 0$$



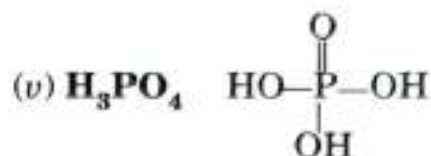
$$m = 7 - 4 - \frac{1}{2} \times 4 = 7 - 6 = +1$$



$$m = 7 - 2 - \frac{1}{2} \times 6 = 7 - 2 - 3 = +2$$



$$m = 7 - 0 - \frac{1}{2} \times 8 = 7 - 4 = +3$$



$$m = 5 - 0 - \frac{1}{2} \times 8 = 5 - 4 = +1$$

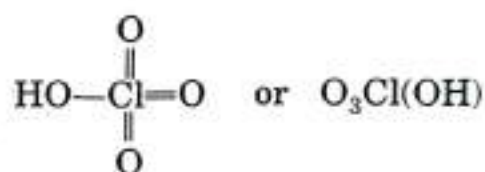
5. Ricci's Formula for Calculating pK_a Values of Oxoacid, $\text{O}_m\text{E}(\text{OH})_n$.

pK_a value of an oxoacid represented by the formula, $\text{O}_m\text{E}(\text{OH})_n$ is given by Ricci's formula given below.

$$\text{pK}_a = 8 - 9m + 4n$$

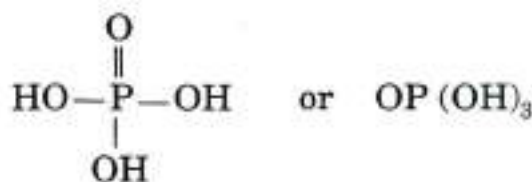
where m = formal charge on the central atom (E) of the acid and n = No. of non-hydroxyl O-atoms in the acid.

Examples (i) HClO_4 molecule. The structure of HClO_4 molecule is given in the margin. This structure shows that for HClO_4 molecule $m = +3$ and $n = 3$. Hence: pK_a value for HClO_4 molecule = $8 - 9 \times 3 + 4 \times 3 = -7$



Structure of HClO_4 molecule ($m = +3, n = 3$)

(ii) H_3PO_4 molecule. The structure of H_3PO_4 molecule is given in the margin. This structure shows that for H_3PO_4 molecule $m = +1$ and $n = 1$. Hence pK_a value for H_3PO_4 molecule = $8 - 9 \times 1 + 4 \times 1 = +3$



Structure of H_3PO_4 molecule ($m = +1, n = 1$)

Factors Affecting the Acidic Strength of Bronsted Acids and Basic Strength of Bronsted Bases

Some of the factors which affect the acidic strength of Bronsted acids and basic strength of Bronsted bases are discussed below:

1. Effect of Solvent

The effect of solvent on the acidic and basic strength is discussed under the following heads:

(i) Effect of solvent on the acid strength of Bronsted acids: Concept of levelling solvent and levelling effect. The relative order of acid strength of various Bronsted acids depends on the extent to which the various acids ionise in a given solvent which acts as a base. The solvent acts as a base, since it accepts a proton donated by the Bronsted acid. The acid strength of a Bronsted acid is its capacity to donate a proton to a base (solvent). As an example let us compare the acid strength the strong acids *viz* HClO_4 , HBr , H_2SO_4 , HCl and HNO_3 in water solvent. All these acids ionise in H_2O (water acts as a base) almost completely to produce H_3O^+ ion.

<i>Acid</i>		<i>Base (Solvent)</i>	\longrightarrow	<i>Acid (Cation of the solvent)</i>		<i>Base</i>
HClO ₄	+	H ₂ O	\longrightarrow	H ₃ O ⁺	+	ClO ₄ ⁻
HBr	+	H ₂ O	\longrightarrow	H ₃ O ⁺	+	Br ⁻
H ₂ SO ₄	+	H ₂ O	\longrightarrow	H ₃ O ⁺	+	HSO ₄ ⁻
HCl	+	H ₂ O	\longrightarrow	H ₃ O ⁺	+	Cl ⁻
HNO ₃	+	H ₂ O	\longrightarrow	H ₃ O ⁺	+	NO ₃ ⁻

Since all the acids ionise in H₂O (solvent) to the same extent (or since all the acids are *completely ionised* to produce H₃O⁺), these strong acids in aqueous solution appear almost equally strong, *i.e.* in aqueous solution these acids behave as being equally strong. Obviously the relative acid strength of these acids cannot be measured in aqueous solution. This phenomenon due to which acids appear to be equally strong is known as **levelling effect** of the solvent (Here the solvent is H₂O) on the acids. The solvent (*i.e.* H₂O) in which the acids appear equally strong is known as **levelling solvent**. Obviously H₂O acts as a levelling solvent for strong acids mentioned above.

The solvent in which given acids / bases ionise completely and appear to be equally strong is called a levelling solvent for the acid and bases. For example

(a) Liq. NH₃ acts as a levelling solvent for the acids HCl (strong acid) and CH₃COOH (weak acid), since these acids ionise completely in liq NH₃ to give NH₄⁺ (ammoniated proton) cation (cation of the solvent, NH₃)

<i>Acid</i>		<i>Base (Levelling solvent)</i>		<i>Acid (Cation of the solvent)</i>		<i>Base</i>
HCl (<i>strong</i>)	+	NH ₃	$\xrightarrow{\text{Complete ionisation}}$	NH ₄ ⁺	+	Cl ⁻
CH ₃ COOH (<i>weak</i>)	+	NH ₃	$\xrightarrow{\text{Complete ionisation}}$	NH ₄ ⁺	+	CH ₃ COO ⁻

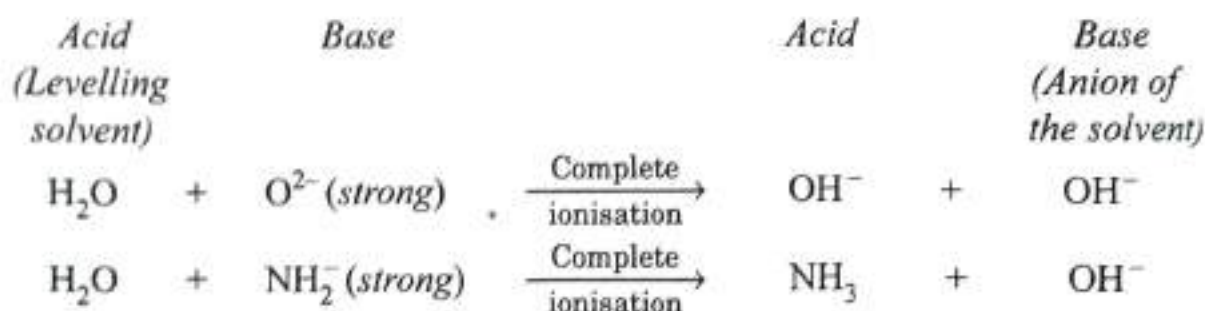
Although HCl is a strong acid and CH₃COOH is a weak acid, yet these acids due to their complete ionisation in liq. NH₃ appear to be equally strong in NH₃ solvent which acts as a levelling solvent for these acids. The acid strength of HCl and CH₃COOH cannot be measured in the levelling solvent for these acids.

(b) CH₃COOH acts as a levelling solvent for the bases C₆H₅NH₂ (weak base) and NaOH (strong base), since these bases ionise completely in CH₃COOH to give CH₃COO⁻ anion (anion of the solvent, CH₃COOH)

<i>Acid (Levelling solvent)</i>		<i>Base</i>		<i>Acid</i>		<i>Base (Anion of the solvent)</i>
CH ₃ COOH	+	C ₆ H ₅ NH ₂ (<i>weak</i>)	$\xrightarrow{\text{Complete ionisation}}$	C ₆ H ₅ NH ₃ ⁺	+	CH ₃ COO ⁻
CH ₃ COOH	+	NaOH (<i>strong</i>)	$\xrightarrow{\text{Complete ionisation}}$	NaOH ₂ ⁺	+	CH ₃ COO ⁻

Although $C_6H_5NH_2$ is a weak base and NaOH is a strong base, yet these bases, due to their complete ionisation in CH_3COOH appear to be equally strong in CH_3COOH which acts as a levelling solvent for these bases. The base strength of $C_6H_5NH_2$ and NaOH cannot be measured in the levelling solvent for these bases.

(ii) Effect of solvent on the base strength of bronsted bases The relative order of the base strength of various Bronsted bases depends on the extent to which the various bases ionise in a given solvent which act as an acid. The solvent acts as an acid, since it donates a proton to the base. The base strength of a Bronsted base is its capacity to accept a proton from the acid (solvent). As an example let us compare the base strength of the strong bases *viz* O^{2-} and NH_2^- in H_2O solvent. Both these bases ionise in solvent H_2O (water acts as an acid) almost completely to produce OH^- ions



Since both the bases ionise in H_2O (solvent) to the same extent (or since both the bases are completely ionised to produce OH^-), these strong bases in aqueous solution appear almost equally strong, i.e. in aqueous solution these bases behave as being equally strong. Obviously the relative base strength of these bases cannot be measured in aqueous solution. It should be easy to understand that H_2O acts as a levelling solvent for the strong bases.

Explanation of levelling effect of a solvent on the basis of solvent system concept of acids and bases According to solvent-system concept of acids and bases, the acids which are stronger than the characteristic cation of the solvent are completely ionised in the solvent to produce the characteristic cation of the solvent and hence the acids appear equally strong in that solvent.

If H_2O is used as solvent, then the characteristic cation of this solvent is H_3O^+ . Similarly according to solvent-system concept of acids and bases, the bases which are stronger than the characteristic anion of the solvent are completely ionised in the solvent to produce the characteristic anion of the solvent and hence the bases appear equally strong in that solvent. If H_2O is used as solvent, then the characteristic anion of this solvent is OH^- .

Examples (i) We have shown above that the strong acids *viz* $HClO_4$, HBr , H_2SO_4 , HCl and HNO_3 appear equally strong in solvent, H_2O . This behaviour of acids is due to the fact that, since these acids are stronger than the characteristic cation (H_3O^+) of the solvent (H_2O), these acids are completely ionised in H_2O solvent to produce H_3O^+ which is the characteristic cation (H_3O^+) of the solvent (H_2O). Due to the complete ionisation of these acids, these acids appear equally strong in solvent (H_2O).

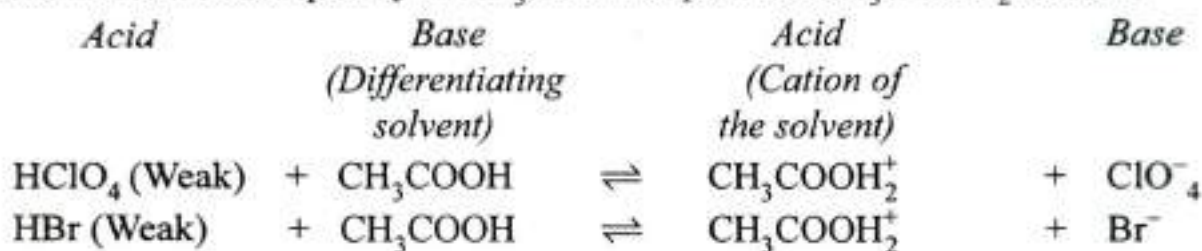
(ii) We have shown above that the strong bases namely O^{2-} and NH_2^- appear equally strong in solvent, H_2O . This behaviour of bases is due to the fact that since

these bases are stronger than the characteristic anion (OH^-) of the solvent (H_2O), these bases are completely ionised in H_2O to produce OH^- which is the characteristic anion of the solvent (H_2O). Due to the complete ionisation of the bases, these bases appear equally strong in solvent (H_2O).

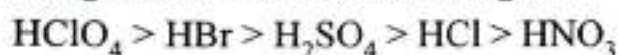
Differentiating solvents. The solvents in which the acids and bases ionise to different extents so that the relative strengths of the acids and bases can be measured are known as differentiating solvents for these acids and bases.

Examples (i) CH_3COOH is a differentiating solvent for strong acids like HClO_4 , HBr , H_2SO_4 , HCl and HNO_3 , since in CH_3COOH solvent these acids ionise to different extents.

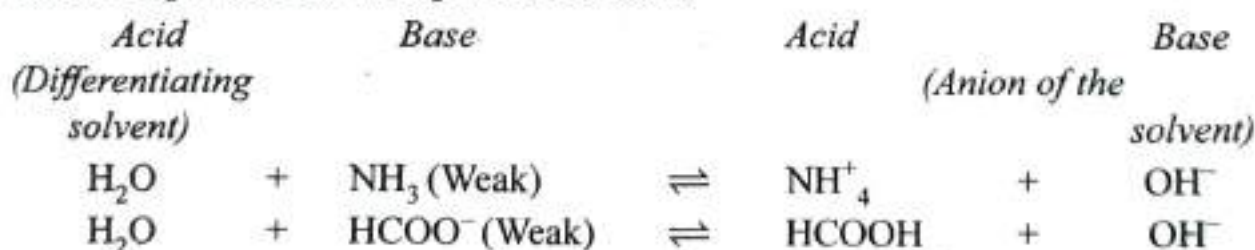
Thus these acids remain in equilibrium in CH_3COOH solvent. In other words these acids do not ionise completely in CH_3COOH to produce $\text{CH}_3\text{COOH}_2^+$ cations.



In the present case since HClO_4 and HBr are weaker acids than the characteristic cation ($\text{CH}_3\text{COOH}_2^+$) of the solvent (CH_3COOH), these acids remain in equilibrium in CH_3COOH solvent. Hence the acid strength of these acids can be measured in CH_3COOH solvent. The given acids have been arranged in the following decreasing order of their acid strength.



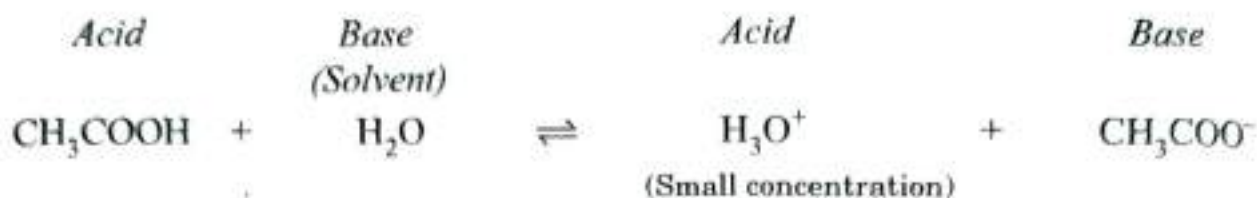
(ii) Now let us consider the ionisation of the bases like NH_3 and HCOO^- in H_2O (solvent). These bases do not get ionised completely in H_2O to produce OH^- ions but exist in equilibrium in aqueous solution.



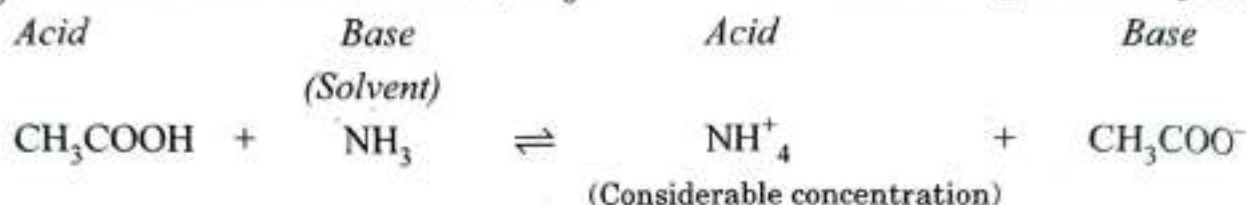
Thus we see that NH_3 and HCOO^- ionise in solvent (H_2O) to different extent. Hence the basic strength of these bases can be measured in H_2O . Consequently H_2O acts as a differentiating solvent for NH_3 and HCOO^- bases. In the present case since NH_3 and HCOO^- are weaker bases than the characteristic anion (OH^-) of the solvent (H_2O), these bases remain in equilibrium in aqueous solution.

Behaviour of a given species as an acid or as a base in different solvents. According to solvent-system of acid and bases, whether a given species will behave as an acid or as a base in the given solvent depends on the acidic or basic character of the solvent. For example:

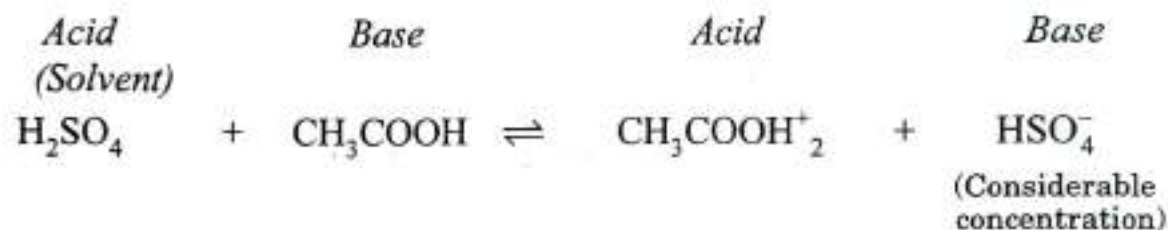
(i) In H_2O since CH_3COOH gives H_3O^+ cations (cations of the solvent, H_2O) of small concentration, this acid behaves as a weak acid in H_2O .



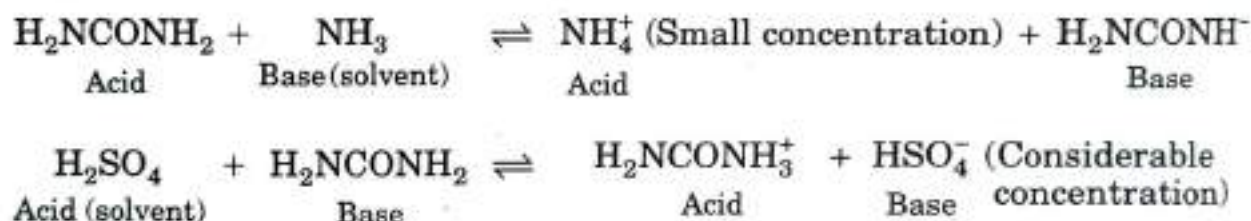
(ii) In liq. NH_3 , since CH_3COOH gives NH_4^+ cations (cations of the solvent, NH_3) of considerable concentration, CH_3COOH behaves as a strong acid in liq. NH_3 .



(iii) In H_2SO_4 , since CH_3COOH gives HSO_4^- ions (anions of the solvent, H_2SO_4) of considerable concentration, CH_3COOH behaves as a base in H_2SO_4 .



(iv) Urea (H_2NCONH_2) behaves as a weak acid in NH_3 but as a strong base in H_2SO_4 .



2. Effect of the Dielectric Constant (ϵ) and Polarity of the Solvent

The acidic and basic strength of an ionic species (solute) dissolved in a solvent increase with an increase in the dielectric constant (ϵ) or polarity of the solvent in which the species has been dissolved.

Explanation. According to coulomb's law, the force of attraction (F) between two ions of a solute having opposite charges q_1 and q_2 is given by:

$$F = \frac{q_1 q_2}{\epsilon r^2},$$

where ϵ is dielectric constant of the solvent and r is the distance between the ions. This relation shows that in solvents having lower value of ϵ , the force of attraction (F) between the ions of the solute would be relatively large and consequently the extent of dissociation of the solute into ions in the solvent would be small. On the other hand, in solvent having high value of ϵ , the force of attraction (F) between the ions of the solute would be relatively small and hence the extent of dissociation of the solute would be large. From this discussion, we can conclude that the acidic strength of acids (solute) and basic strength of bases (solute) would increase with the increase in the value of ϵ of the solvent.

Now since the dielectric constant (ϵ) and dipole moment are directly related with each other, *greater is the dielectric constant or polarity of the solvent, greater would be the acidic or basic strength of the species dissolved in that solvent.*

3. Effect of Electron Withdrawing and Electron-Donating Substituents or Groups

Electron-withdrawing and electron-donating nature of substituents present in acids and bases have marked effect on the relative strength of acids and bases.

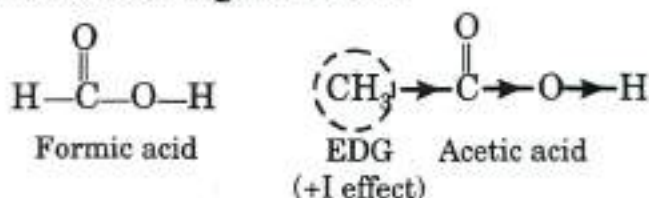
An electron withdrawing substituent or group (EWG) present in a species has electron-withdrawing inductive effect ($-I$ effect). The presence of EWG in a species increases the acidic strength of the species. An electron-donating substituent or group (EDG) present in a species has electron-donating inductive effect ($+I$ effect). The presence of EDG in a species decreases the acidic strength of the species.

Similarly the presence of EWG in a species decreases the basic strength of the species and the presence of an EDG increases the basic strength of the species.

How the presence of an EWG or EDG in an acid or a base affects the acidic strength of acids and basic strength of bases can be explained by considering the following examples:

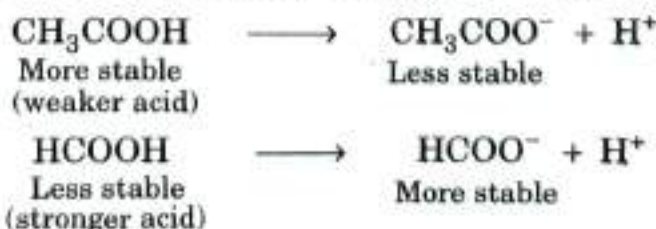
(i) *Formic acid (HCOOH) is a stronger acid than acetic acid (CH₃COOH).* This can be explained as follows:

The structures of these acids are given below:



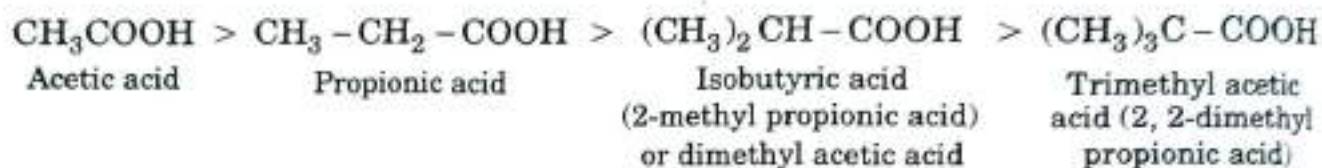
In CH₃COOH molecule, methyl group ($-\text{CH}_3$) is an electron-donating group (EDG) and hence has electron-donating inductive effect ($+I$ effect). Because of $+I$ effect of $-\text{CH}_3$ group present in CH₃COOH, this group donates electrons to O-H bond in CH₃COOH molecule. As a result, the electron density on O-atom in O-H bond in CH₃COOH increases. Due to the increase in electron density on O-atom, it becomes more difficult for CH₃COOH molecule to release H⁺ ions as compared to HCOOH. Thus HCOOH can release H⁺ ions more easily as compared to CH₃COOH and is a stronger acid than CH₃COOH.

Further, $+I$ effect of CH₃ group intensifies (increases) the magnitude of negative charge (electron density) on carboxylate anion (CH₃COO⁻) present in CH₃COOH and thus makes CH₃COO⁻ anion of CH₃COOH less stable as compared to HCOO⁻ anion present in HCOOH. This decreases the acidic strength of CH₃COOH.



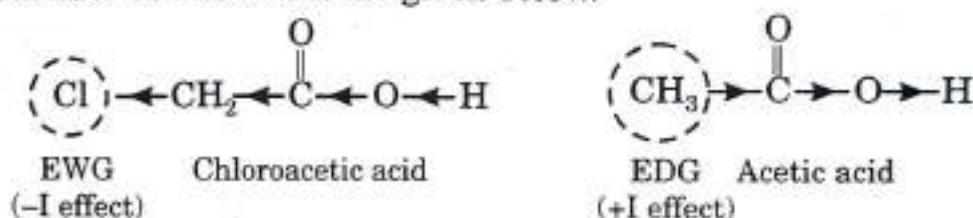
(ii) Acidic strength of $\text{CH}_3\text{-COOH}$, $\text{CH}_3\text{-CH}_2\text{-COOH}$, $(\text{CH}_3)_2\text{CH-COOH}$ and $(\text{CH}_3)_3\text{C-COOH}$ decreases in the order: $\text{CH}_3\text{-COOH} > \text{CH}_3\text{-CH}_2\text{-COOH} > (\text{CH}_3)_2\text{CH-COOH} > (\text{CH}_3)_3\text{C-COOH}$. This order can be explained as follows:

We know that greater is the magnitude of +I effect of an alkyl group, lower is the acidic strength of the acid containing the alkyl group. Thus since +I effect of alkyl groups namely $\text{CH}_3\text{-}$, $\text{CH}_3\text{-CH}_2\text{-}$, $(\text{CH}_3)_2\text{CH-}$, $(\text{CH}_3)_3\text{C-}$ increases in the order: $\text{CH}_3\text{-} < \text{CH}_3\text{-CH}_2\text{-} < (\text{CH}_3)_2\text{CH-} < (\text{CH}_3)_3\text{C-}$, the relative acid strength of carboxylic acids containing these alkyl groups decreases in the same order as shown below.



(iii) Chloroacetic acid ($\text{Cl-CH}_2\text{-COOH}$) is a stronger acid than acetic acid (CH_3COOH). This can be explained as follows:

The structures of these acids are given below.



-Cl group present in ClCH_2COOH is an electron-withdrawing group (EWG) and hence has electron-withdrawing inductive effect (-I effect). Because of -I effect of -Cl group, this group withdraws electrons from the O-H bond. As a result, the electron density in O-H bond in ClCH_2COOH decreases and O-H bond weakens. In other words it becomes easier for ClCH_2COOH molecule to release H^+ ions as compared the CH_3COOH . Thus ClCH_2COOH is a stronger acid than CH_3COOH .

Further -I effect of -Cl group disperses (decreases) the magative charge (electron density) on $\text{ClCH}_2\text{COO}^-$ ion as compared to ClCH_2COOH and thus makes $\text{ClCH}_2\text{COO}^-$ ion more stable as compared ClCH_2COOH



Since - CH_3 group in CH_3COOH is an electron-donating group (EDG), it has electron-donating inductive effect (+I effect). Because of +I effect of - CH_3 group, this group intensities (increases) the negative charge (electron density) on CH_3COO^- ion as compared to CH_3COOH and thus makes CH_3COO^- ion less stable as compared to CH_3COOH .



It is because of -I effect of -Cl group and +I effect of - CH_3 group that ClCH_2COOH is a stronger acid than CH_3COOH .

Above discussion can be summarised by stating that $-Cl$ group in $ClCH_2COOH$ decreases ($-I$ effect) the negative charge on $ClCH_2COO^-$ and hence increases the stability of $ClCH_2COO^-$ as compared to $ClCH_2COOH$. On the other hand, $-CH_3$ group increases ($+I$ effect) the negative charge on CH_3COO^- ion and hence decreases the stability of CH_3COO^- in as compared to CH_3COOH .

(iv) *The acidic strength of BH_3 , BF_3 and BMe_3 molecules increases in the order: $BMe_3 < BH_3 < BF_3$. This can be explained as follows:*

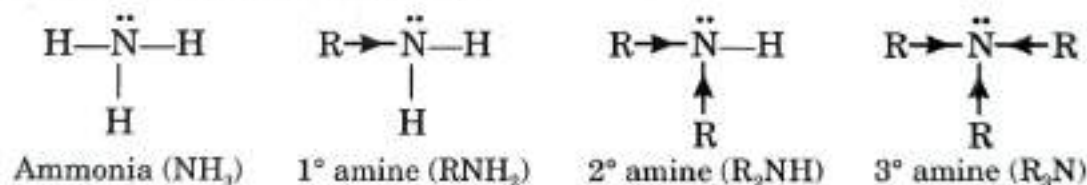
The central B-atom in each of the compounds has vacant $2p$ orbital and hence each of these compounds acts as Lewis acid. Since methyl group (Me) is an electron-donating group, the presence of this group in Me_3B decreases the acidity of Me_3B w.r.t. that of BH_3 . Similarly, since F^- ion is an electron-withdrawing group, it will increase the acidity of BF_3 as compared to that BH_3 . Thus Me_3B is the weakest acid, BF_3 is the strongest acid and BH_3 has intermediate acidic strength, *i.e.* the order of acidic strength is $Me_3B < BH_3 < BF_3$.

(v) *C_6H_5COOH is a stronger acid than CH_3COOH . This can be explained as follows:*

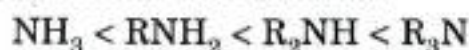
C_6H_5COOH is stronger acid than CH_3COOH because phenyl group ($-C_6H_5$) present in C_6H_5COOH is an EWG whereas $-CH_3$ group present in CH_3COOH is an EDG.

(vi) *Basic strength of NH_3 and aliphatic amines (RNH_2 , R_2NH and R_3N) in gas phase (non-aqueous solvent) increases in the order: $NH_3 < RNH_2 < R_2NH < R_3N$. This can be explained as follows:*

Due to the presence of electron-donating alkyl groups in amines, the electron density on N-atom increases ($+I$ effect) as we proceed as $NH_3 \rightarrow RNH_2$ (1° amine) $\rightarrow R_2NH$ (2° amine) $\rightarrow R_3N$ (3° amine). Due to the increase in electron density on N-atom, it becomes more easy for amines to donate the lone pair of electrons than NH_3 as we move from RNH_2 to R_3N .



Thus the basic strength of amines increases as :



or $NH_3 < 1^\circ \text{ amine} < 2^\circ \text{ amine} < 3^\circ \text{ amine}$

Since the solvation effect, *i.e.* stabilisation of conjugate acid due to H-bonding is absent in amines in gas phase, the basic strength of amines in gas phase depends only on $+I$ effect of alkyl groups.

(vii) *$C_6H_5NH_2$ is a weaker base than NH_3 . This can be explained as follows:*

Since $-C_6H_5$ group (phenyl group) is an electron-withdrawing group, this group decreases the electron density on N-atom in $C_6H_5NH_2$ molecule. The decrease in electron density on N-atom makes $C_6H_5NH_2$ weaker base than NH_3 .

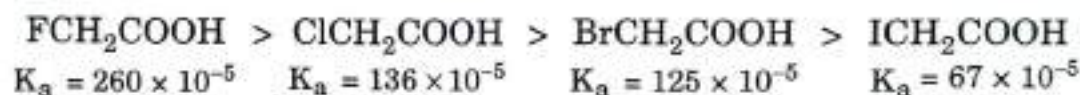
(viii) Diphenylamine $[(C_6H_5)_2NH]$ is a weaker base than aniline $(C_6H_5NH_2)$. This can be explained as follows:

Diphenylamine, $(C_6H_5)_2NH$ and aniline, $C_6H_5NH_2$ both contain negative $-C_6H_5$ groups which are electron-withdrawing groups. $(C_6H_5)_2NH$ contains two $-C_6H_5$ groups and $C_6H_5NH_2$ has only one $-C_6H_5$ group. Thus in $(C_6H_5)_2NH$ lp of electrons on N-atom is distributed over two $-C_6H_5$ groups while in $C_6H_5NH_2$ lp of electrons on N-atom is distributed only over one $-C_6H_5$ group. Hence in $(C_6H_5)_2NH$ molecule the electron density of lp of electrons on N-atom is decreased. The decrease in electron density makes $(C_6H_5)_2NH$ weaker base than $C_6H_5NH_2$.

4. Effect of the Magnitude of $-I$ Effect Exerted by Electron-Withdrawing Substituent

Examples (i) In case of α -halo acetic acids, greater is the magnitude of electron-withdrawing inductive effect ($-I$ effect) of halogen group, greater is the acidic strength of halo acetic acids.

We know that α -haloacetic acids are FCH_2COOH (fluoroacetic acid), $ClCH_2COOH$ (chloroacetic acid), $BrCH_2COOH$ (bromoacetic acid) and ICH_2COOH (iodoacetic acid). All the acids have halogen group which has $-I$ effect. Now since electronegativity of halogen atoms decreases as $F > Cl > Br > I$, the magnitude of $-I$ effect exerted by halogens also decreases in the same order ($F > Cl > Br > I$). Due to the decrease in the magnitude of $-I$ effect of halogens, acidic strength of halo acetic acids decreases as:



(ii) The acidic strength of CH_3CH_2OH , CF_3CH_2OH and CCl_3CH_2OH decreases in the order: $CF_3CH_2OH > CCl_3CH_2OH > CH_3CH_2OH$. This decreasing order can be explained as follows.

Since $CH_3 - CH_2$ group (ethyl group) is an electron-releasing group ($+I$ effect), the presence of this group in CH_3CH_2OH makes $O-H$ bond strong and hence the release of a proton (H^+) from CH_3CH_2OH becomes difficult, i.e. CH_3CH_2OH is the weakest acid. We know that F and Cl both have electron-withdrawing ability ($-I$ effect). Now since the electron-withdrawing ability of F is higher than that of Cl , $O-H$ bond in CF_3CH_2OH weakens and the release of a proton (H^+) from this acid becomes comparatively more easy than from CCl_3CH_2OH . Consequently CF_3CH_2OH is stronger acid than CCl_3CH_2OH . CF_3CH_2OH is stronger acid than CCl_3CH_2OH . CH_3CH_2COOH is the weakest acid. Thus the order of acidity of the given acids is:



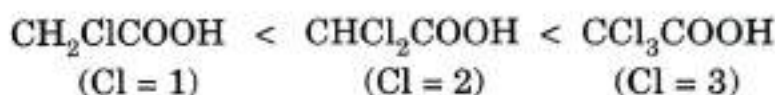
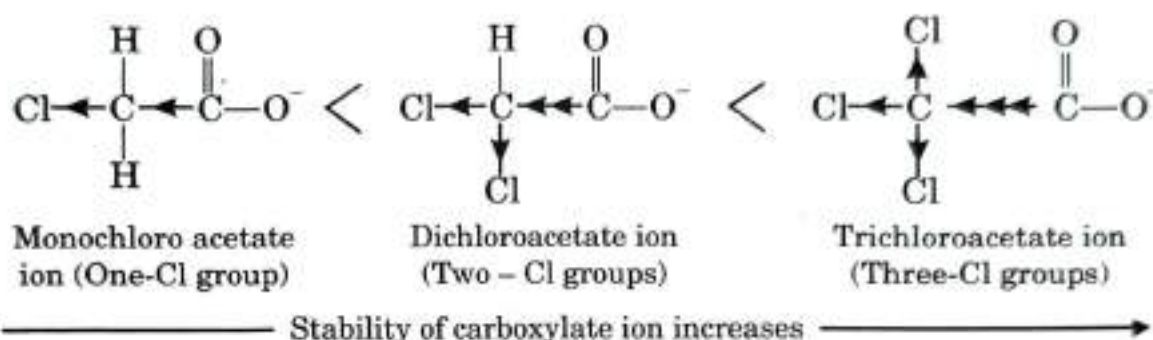
5. Effect of the Number of Electron-Withdrawing Substituents

Examples (i) In case of chloro acetic acids, higher is the number of electron-withdrawing groups ($-Cl$ groups) present in the chain attached with carboxyl group, greater is the acidic strength of chloroacetic acid.

It has been observed that the acidic strength of the three chloroacetic acids increases in the following order:

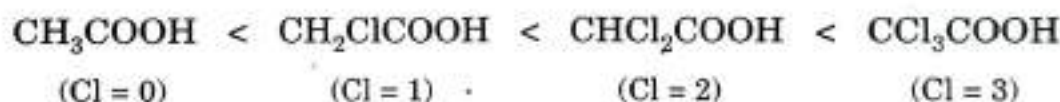


We know that since $-\text{Cl}$ group is an electron-withdrawing group (EWG), it has $-I$ effect. Due to $-I$ effect of $-\text{Cl}$ group, the dispersal of negative charge on carboxylate ion increases with the increase in the number of $-\text{Cl}$ groups. This increases the stability of carboxylate ion and hence the acidic strength of the corresponding chloro acetic acid increases.



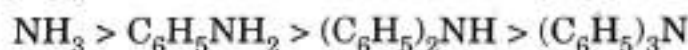
————— Acidic strength increases —————>

Since CH_3COOH has no $-\text{Cl}$ group, it is the weakest acid of all the chloroacetic acids. Thus:



————— Acidic strength increases —————>

(ii) The basic strength (basicity) of ammonia (NH_3), phenylamine ($\text{C}_6\text{H}_5\text{NH}_2$), diphenyl amine [$(\text{C}_6\text{H}_5)_2\text{NH}$] and triphenylamine [$(\text{C}_6\text{H}_5)_3\text{N}$] decreases in the order:



This decreasing order can be explained as follows:

Explanation. NH_3 has no electron-withdrawing group and hence has the maximum basicity. On the other hand, each of the remaining substituted amines has one, two and three electron-withdrawing phenyl ($-\text{C}_6\text{H}_5$) groups. The presence of these groups decreases the basicity of the substituted amines. Greater is the number of electron-withdrawing groups, lesser is the basicity. Thus the basicity of the given compounds is in the order:

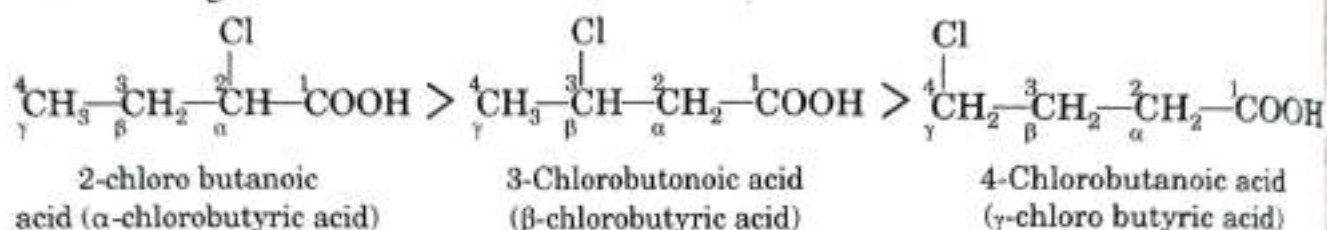


6. Effect of the Distance of the Electron-Withdrawing Substituent from Carboxyl Group in an Aliphatic Carboxylic Acid

As the distance of the electron-withdrawing substituent from the carboxyl group present in an aliphatic carboxylic acid increases, $-I$ effect exerted by the substituent decreases and hence the dispersal of negative charge of carboxylate ion becomes

less pronounced. This decreases the stability of the carboxylate ion and, therefore, the acid strength of the acids decreases.

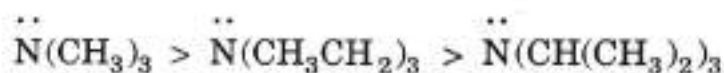
Example. The acid strength of chloro substituted butanoic acids decreases in the following order:



The highest acidic strength of 2-chloro butanoic acid is because of the fact that the distance between $-\text{Cl}$ group (electron-withdrawing group) and COOH is minimum. The lowest acidic strength of 4-chlorobutanoic acid is because the distance between $-\text{Cl}$ group and COOH is the maximum.

7. Effect of Steric Overcrowding of the Substituents

Examples (i) The basic strength of tiralkyl amines decreases in the order:



or Trimethyl amine > Triethylamine > Triisopropyl amine

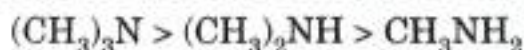
Explanation. As the bulk of the substituent goes on increasing, the steric overcrowding of the substituent around the electron pair on N-atom of amines also increases. As a result, the approach of an electron acceptor (acid) towards the electron pair on N-atom goes on becoming more and more difficult and hence basic strength of amines goes on decreasing.

(ii) $(\text{CH}_3)_3\text{N}$ is less basic than $(\text{CH}_3)_2\text{N}$

Explanation. $(\text{CH}_3)_3\text{N}$ is less basic than $(\text{CH}_3)_2\text{N}$ because the steric overcrowding of the three CH_3 groups (electron-releasing groups) round N-atom in $(\text{CH}_3)_3\text{N}$ molecule makes the bonding of N-atom of this molecule with proton relatively difficult.

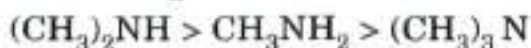
8. Solvation Effects

We have already shown that the basic strength of 1° , 2° and 3° amines in gas phase decreases in the order (Here we have considered methyl amines)



or 3° amine > 2° amine > 1° amine

but in aqueous solution the basic strength of the above amines decreases in the order:



or 2° amine > 1° amine > 3° amine.

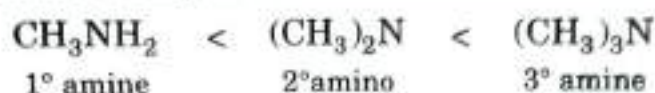
or Secondary amine > Primary amine > Tertiary amine

Explanation. The above decreasing order of basic strength of amines in aqueous solution can be explained as follows:

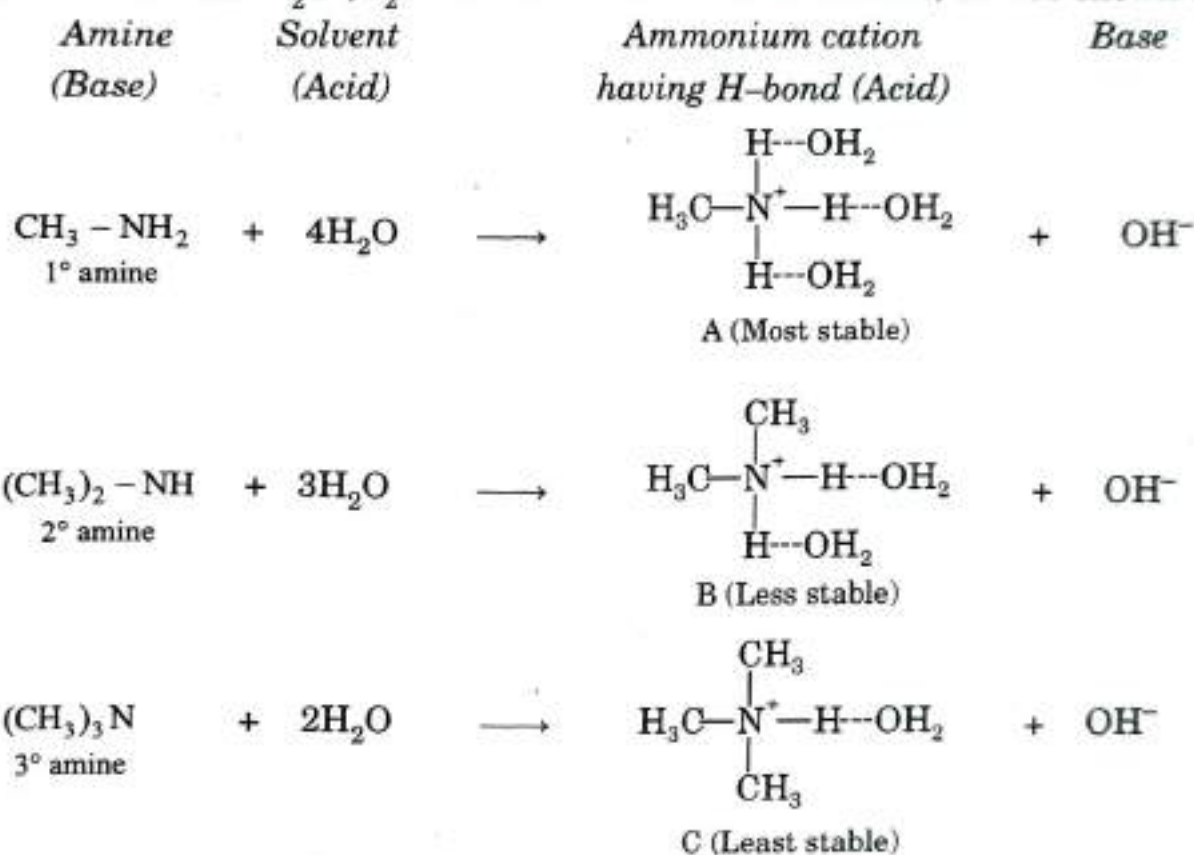
The basic strength of an amine in aqueous solution depends on the stability of ammonium cation or conjugate acid formed by the amine by accepting a proton

(H⁺) from H₂O. The stability of the ammonium cation, in turn, depends on the following factors.

(a) *+I effect of alkyl groups.* As the number of alkyl groups (here alkyl groups are CH₃ groups) increases, due to +I effect of alkyl groups, the dispersal of positive charge on the ammonium cation increases. Due to the increase in the dispersal of positive charge, the basic strength of amines also increases in the order.



(b) *Stability of ammonium cations derived from amines due to H-bonding (Solvation effect).* The formation of ammonium cations obtained by the reaction of three amines with H₂O (H₂O acts as an acid towards amines) can be shown as:



Ammonium cations derived from CH₃NH₂, (CH₃)₂NH and (CH₃)₃N amines are CH₃NH₃⁺(H₂O)₃ (A), (CH₃)₂NH₂⁺(H₂O)₂ (B) and (CH₃)₃NH⁺(H₂O) (C) respectively. These cations are obtained due to H-bonding between H-atom of amines and O-atom of H₂O molecules. The number of H-bonded H-atoms in these cations decreases as 3 (in A) > 2 (in B) > 1 (in C). Due to the decrease in the number of H-bonded H-atoms, the stability of A, B and C cations decreases in the same order: A (Most stable) > B > C (Least stable)

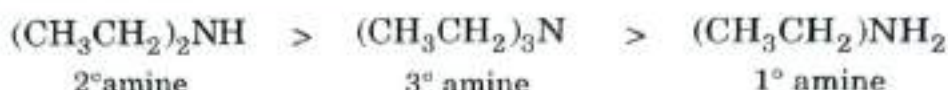
If we consider the combined effect of +I effect and H-bonding effect due to solvation, the relative order of basic strength of methyl amines, in aqueous solution is found to decrease as:



or

This order is true only when alkyl group is CH₃ group.

Steric hinderance of alkyl groups to H-bonding. If the alkyl group is bigger than CH_3 group (e.g. ethyl, propyl etc), there will be some steric hinderance to H-bonding. As a result, the relative order of basic strength of amines in aqueous solution is found to decrease as:



When alkyl group is a CH_3 group, there is no hinderance of this group to H-bonding.

9. Charge on the Species and Charge-to-Size Ratio: Acidic Strength of Hydrated Metal Ions

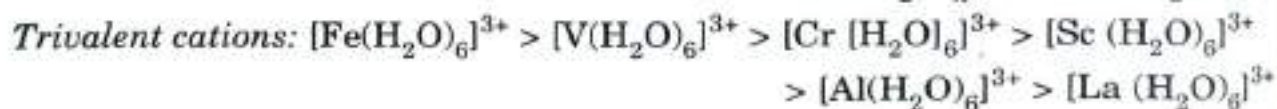
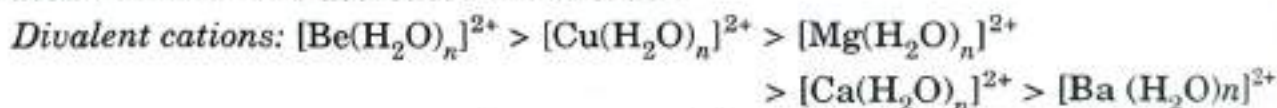
An increase in the positive charge on a species would increase the acidic strength of the species because the increase in positive charge increases the electron-accepting capacity of the species. An increase in the negative charge on a species would increase the basic strength of the species because an increase in negative charge increases the electron-donating capacity of the species.

Examples (i) Hydrated metal ion, $[\text{M}(\text{H}_2\text{O})_6]^{n+}$ releases H_3O^+ ions in aqueous solution and hence behaves as acid.



Since $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion has greater positive charge (= +3) than $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (= +2), the former is a stronger acid than the latter. Similarly $[\text{Ni}(\text{OH})_4]^{2-}$ ion (negative charge = -2) is a stronger base than $[\text{Ni}(\text{OH})_4]^{-}$ (negative charge = -1)

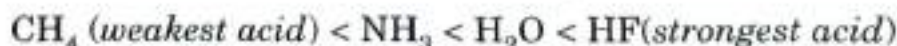
(ii) The acidity of hydrated metal cations having the same positive charge is determined by their charge-to-size ratio value. Larger is the charge-to-size ratio of a hydrated metal cation, more polar is O-H bond in the coordinated H_2O in the hydrated cation and hence more easily a proton (H^+) is released as H_3O^+ . On the basis of charge-to-size ratio, the acidic strength of some divalent and trivalent hydrated metal cations decreases in the order:



10. Effect of Electronegativity (EN)

Following examples show how the electronegativity of elements present in given species affects the acidic strength of the species.

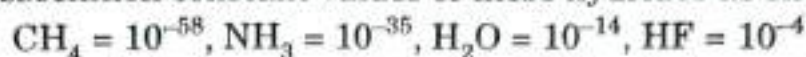
Examples. (i) The acidic strength of CH_4 , NH_3 , H_2O and HF increases in the under:



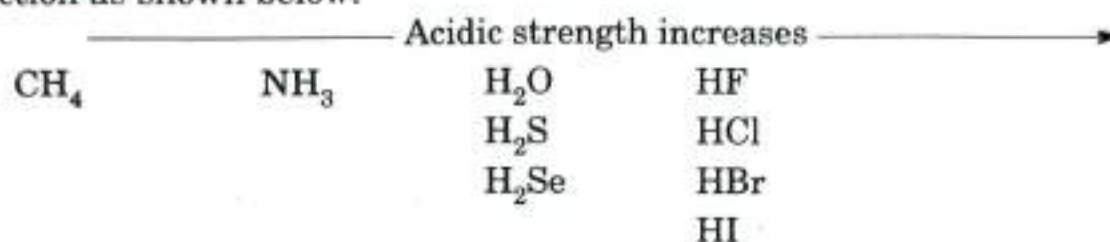
This increasing order can be explained on the basis of electronegativity values of the non-metals present in the given hydrides. Higher is the electronegativity of the non-metal in the given hydride, easier would be the release of proton (H^+) from the hydride. In other words, the acid strength (proton releasing capacity) of hydrides would increase with the increase in electronegativity of non-metal. Now since elec-

Electronegativity of C, N, O and F increases as $C < N < O < F$, the acidic strength of the hydrides also increases in the same order ($CH_4 < NH_3 < H_2O < HF$).

The increase in acidic strength from CH_4 to HF is supported by the successive increase in acid dissociation constant values of these hydrides as shown below.



In general, in a period since the electronegativity of elements increases on moving from left to right, the acidic strength of hydrides also increases in the same direction as shown below.



(ii) Acidic strength of hypohalous acids ($HClO$, $HBrO$ and HIO) decreases as the electronegativity of halogen atoms decreases from F to I. Similarly, the acidic strength of perhalic acids ($HClO_4$, $HBrO_4$ and HIO_4) also decreases with the decrease of EN from Cl to I. Thus:

Hypohalous acids: $HClO > HBrO > HIO$

— EN of halogen decreases \rightarrow

— Acidic strength decreases \rightarrow

Perhalic acids: $HClO_4 > HBrO_4 > HIO_4$

— EN of halogen decreases \rightarrow

— Acidic strength decreases \rightarrow

(iii) Acidic strength of HNO_3 , HPO_3 and $HAsO_3$ decreases in the order: $HNO_3 > HPO_3 > HAsO_3$. The decrease is due to the decrease in EN values of the central atoms ($N > P > As$) as we move down the group from N to As.

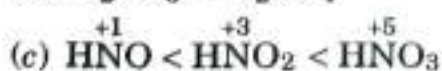
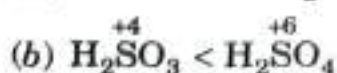
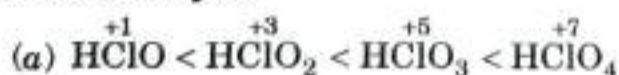
(iv) H_2SO_3 is stronger acid than H_2SeO_3 ($H_2SO_3 > H_2SeO_3$) because of greater electronegativity of S-atom than Se-atom.

(v) Acidic strength of H_3PO_4 , H_3AsO_4 and H_3SbO_4 decreases in the order:

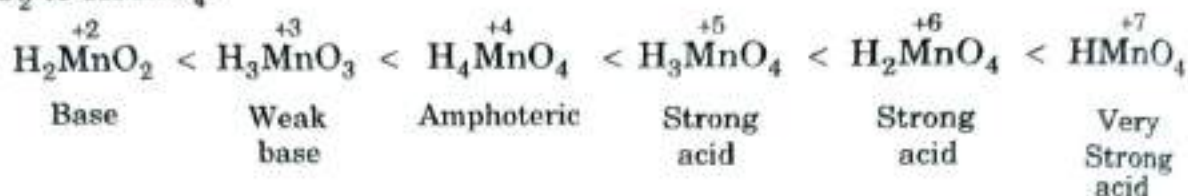
$H_3PO_4 > H_3AsO_4 > H_3SbO_4$. The decrease is due to the decrease in EN value of the central atoms ($P > As > Sb$) as we move down the group from P to Sb.

11. Effect of Oxidation Number (O.N.) of the Central Atom.

(i) In oxoacids, higher is the O.N. of the central atom, greater is the acidic strength of the acid. Higher O.N. increases the electron-pulling capacity of the acid and makes the release of H^+ ions from the acid easier. This is the reason why acidic strength of various oxoacids increases with the increase of O.N. of the central atom. For example:



(ii) Acidic strength of oxo acids of Mn increases in the order shown below. The increasing order is due to the increase in O.N. of Mn atom as we move from H_2MnO_2 to HMnO_4 .



_____ O.N. of Mn atom increases _____ →

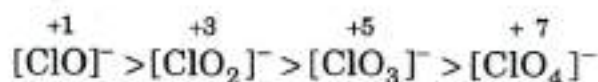
_____ Acidic strength increases _____ →

(iii) Acidic strength of HMnO_4 , H_2MnO_4 and H_3MnO_4 decreases as $\text{HMnO}_4 > \text{H}_2\text{MnO}_4 > \text{H}_3\text{MnO}_4$ due to the decrease in O.N. of Mn atom.

(iv) Acidic strength of H_2SO_3 , H_2SO_4 , HClO_3 and HClO_4 increases as $\text{H}_2\text{SO}_3 < \text{HClO}_3 < \text{H}_2\text{SO}_4 < \text{HClO}_4$. This increasing order is due to the increase in O.N. of the central atom from S to Cl.

(v) The acidic strength of H_2CO_3 , H_3PO_4 , H_2SO_4 and HClO_4 also increases in the order $\text{H}_2\text{CO}_3 < \text{H}_3\text{PO}_4 < \text{H}_2\text{SO}_4 < \text{HClO}_4$. This increasing order is also due to the increase in O.N. of the central atom from C to Cl.

(vi) The basic strength (basicity) of oxo anions *viz.* ClO^- , ClO_2^- , ClO_3^- and ClO_4^- decreases as:



_____ Basic strength decreases _____ →

The decrease in basic strength is due to the increase in O.N. of Cl atom from +1 (in ClO^-) to +7 (in ClO_4^-).

12. Effect of the Number of -OH Groups Per Unhydroxyl O-atom

Greater is the number of -OH groups per unhydroxyl (unprotonated) O-atom in an oxoacid, lesser is the acidic strength of the acid. For example:

(i) $\text{H}_2\text{S}_2\text{O}_7$ is a stronger acid than H_2SO_4 .

Explanation. The structures of $\text{H}_2\text{S}_2\text{O}_7$ and H_2SO_4 are given in Fig. 3.4.

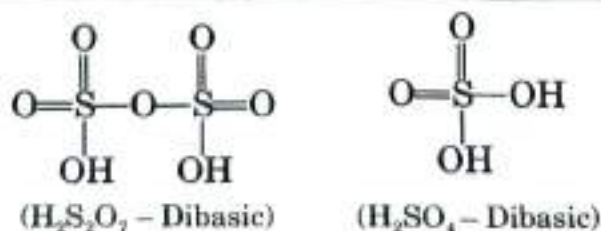
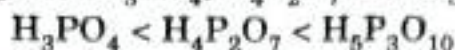


Fig 3.4 Structure of $\text{H}_2\text{S}_2\text{O}_7$ and H_2SO_4 molecules.

These structures show that the number of -OH groups per unhydroxyl O-atom in $\text{H}_2\text{S}_2\text{O}_7$ and H_2SO_4 is equal to $2/4 = 0.5$ and $2/2 = 1.0$ respectively. Since this number is less in $\text{H}_2\text{S}_2\text{O}_7$ than in H_2SO_4 , $\text{H}_2\text{S}_2\text{O}_7$ is a stronger acid than H_2SO_4 ($\text{H}_2\text{S}_2\text{O}_7 > \text{H}_2\text{SO}_4$)

(ii) The acid strength of H_3PO_4 , $\text{H}_4\text{P}_2\text{O}_7$ and $\text{H}_5\text{P}_3\text{O}_{10}$ increases in the order:



Explanation: The structures of H_3PO_4 , $\text{H}_4\text{P}_2\text{O}_7$ and $\text{H}_5\text{P}_3\text{O}_{10}$ are given in Fig 3.5.

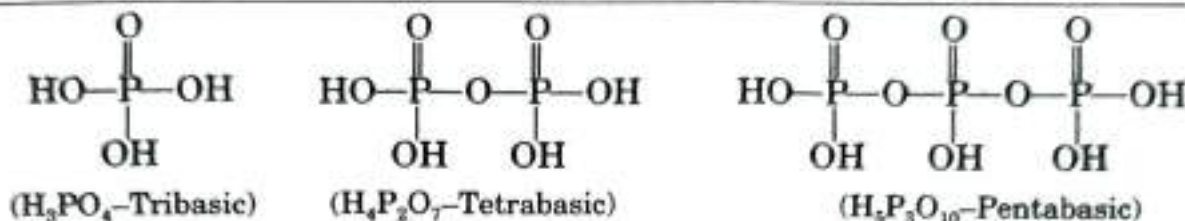


Fig. 3.5 Structure of H_3PO_4 , $\text{H}_4\text{P}_2\text{O}_7$ and $\text{H}_5\text{P}_3\text{O}_{10}$ molecules

These structures show that the number of $-\text{OH}$ groups per unprotonated O-atoms in these acids is as $\text{H}_3\text{PO}_4 = 3$, $\text{H}_4\text{P}_2\text{O}_7 = 4/2 = 2$, $\text{H}_5\text{P}_3\text{O}_{10} = 5/3 = 1.66$. Now since this number *decreases* as $\text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_7 > \text{H}_5\text{P}_3\text{O}_{10}$, the acidic strength of these acids *increases* as $\text{H}_3\text{PO}_4 < \text{H}_4\text{P}_2\text{O}_7 < \text{H}_5\text{P}_3\text{O}_{10}$.

(iii) The acidic strength of H_3PO_2 , H_3PO_3 and H_3PO_4 decreases in the order $\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_4$.

Explanation The structures of H_3PO_2 , H_3PO_3 and H_3PO_4 are given in Fig. 3.6.

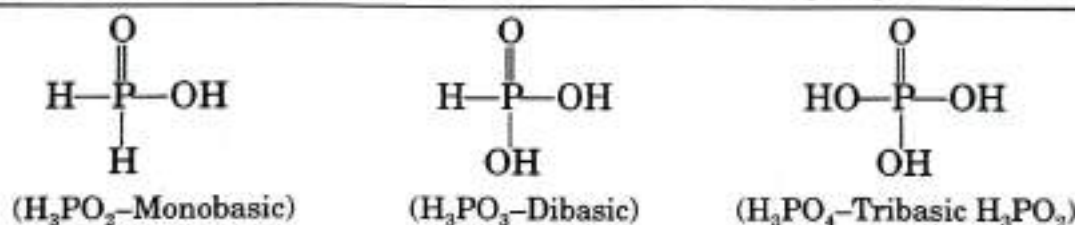


Fig. 3.6 Structure of H_3PO_2 , H_3PO_3 and H_3PO_4 molecules.

These structures show that the number of $-\text{OH}$ groups per unhydroxyl O-atom in H_3PO_2 , H_3PO_3 and H_3PO_4 is equal to 1, 2 and 3 respectively. Since the number of $-\text{OH}$ groups increases as $\text{H}_3\text{PO}_2 < \text{H}_3\text{PO}_3 < \text{H}_3\text{PO}_4$, the acidic strength of these acids decreases as $\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_4$.

(iv) The acidic strength of $\text{ClO}_3(\text{OH})$, $\text{ClO}_2(\text{OH})$, $\text{SO}(\text{OH})_2$ and $\text{SO}_2(\text{OH})_2$ decreases in the order $\text{ClO}_3(\text{OH}) > \text{ClO}_2(\text{OH}) > \text{SO}_2(\text{OH})_2 > \text{SO}(\text{OH})_2$.

Explanation. The structures of the given acids are given in Fig. 3.7.

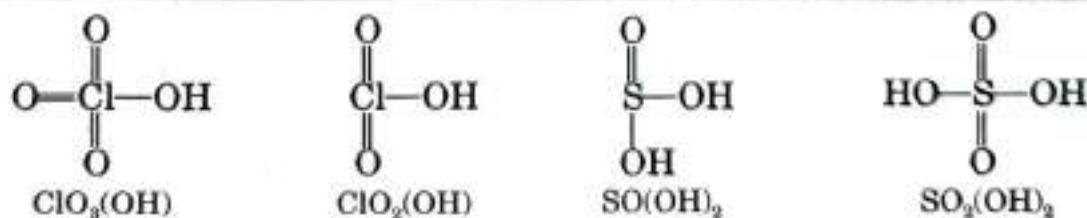


Fig. 3.7 Structure of $\text{ClO}_3(\text{OH})$, $\text{ClO}_2(\text{OH})$, $\text{SO}(\text{OH})_2$ and $\text{SO}_2(\text{OH})_2$ molecules

The structures of the given acids shown in Fig. 3.7 show that the number (n) of $-\text{OH}$ groups per unhydroxyl O-atom in these acids is $\text{ClO}_3(\text{OH}) = 1/3 = 0.33$, $\text{ClO}_2(\text{OH}) = 1/2 = 0.50$, $\text{SO}(\text{OH})_2 = 2$ and $\text{SO}_2(\text{OH})_2 = 2/2 = 1$. Since the value of n for these acids increases as $\text{ClO}_3(\text{OH}) < \text{ClO}_2(\text{OH}) < \text{SO}_2(\text{OH})_2 < \text{SO}(\text{OH})_2$, the acidic strength of these acids decreases as $\text{ClO}_3(\text{OH}) > \text{ClO}_2(\text{OH}) > \text{SO}_2(\text{OH})_2 > \text{SO}(\text{OH})_2$. This order shows that $\text{ClO}_3(\text{OH})$ is the strongest acid and $\text{SO}(\text{OH})_2$ is the weakest acid.

(v) The acidic strength of $O_3Mn(OH)$, $O_2Mn(OH)_2$ and $OMn(OH)_3$ decreases as $O_3Mn(OH) > O_2Mn(OH)_2 > OMn(OH)_3$

Explanation. The structures of the given acids are given in Fig. 3.8.

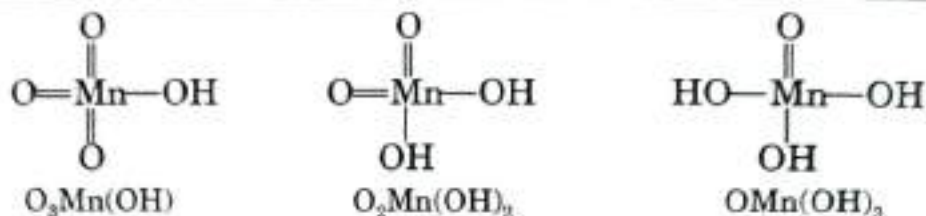
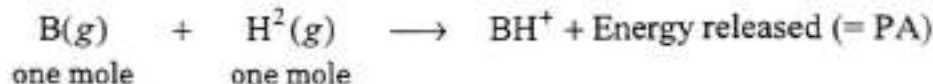


Fig. 3.8 Structure of $O_3Mn(OH)$, $O_2Mn(OH)_2$ and $OMn(OH)_3$ molecules

These structures show that the number of $-OH$ groups (n) per unhydroxylated O-atom in these acids is equal to $O_3Mn(OH) = 1/3$, $O_2Mn(OH)_2 = 2/2 = 1$ and $OMn(OH)_3 = 3$. Since the value of n increases as $O_3Mn(OH) < O_2Mn(OH)_2 < OMn(OH)_3$, the acidic strength of these acids decreases as $O_3Mn(OH) > O_2Mn(OH)_2 > OMn(OH)_3$.

13. Effect of Proton Affinity (PA) Values of Bases in Gaseous Phase

Basic character of a base in gaseous phase is measured in terms of proton affinity (PA) of the base. PA of a base is defined as the energy released when one mole of a base (B) reacts with one mole of protons (H^+), both being in the gaseous state.



As is the practice with EA, PA is also expressed in KJ / mole with a positive sign. Higher is the value of PA of a species, higher is the amount of energy released and hence greater is the basic character of the species.

Basic strength of binary hydrides. PA values of the binary hydrides of the elements of groups 15, 16 and 17 are given in Table 3.2.

Table 3.2 : Proton affinities (in KJ / mole) of some binary hydrides.

Group VA (15)	Group VIA (16)	Group VIIA (17)
PA values decrease \longrightarrow		
NH_3 854 PH_3 789 AsH_3 750 PA values decrease \downarrow	H_2O 697 H_2S 712 H_2Se 717 PA values increase \downarrow	HF 399 HCl 564 HBr 589 HI 628 PA values increase \downarrow

It may be seen that the PA values of binary hydrides decrease on moving from left to right in the hydrides of group 15 to 17. Thus NH_3 has greater affinity for a proton (H^+) to form NH_4^+ ion than H_2O to form H_3O^+ or HF to form HF_2^+ . As a result

Bronsted basicity of binary hydrides decreases along a period with the decrease of their PA values.

As we move down group 15, PA values of the trihydrides decrease. Thus since PA value of NH_3 (= 854 KJ/mole) is greater than that of PH_3 (= 789 KJ/mole), NH_3 would hold on a proton better than PH_3 .

As we move down the hydrides of the elements of groups 16 and 17, PA values increase. This means that the basic strength of the hydrides also increases down the groups. Thus the eagerness of HCl molecule to take up a proton to form H_2Cl^+ is greater than that of HF to form H_2F^+ .

PA values (in KJ/mole) of NH_3 , CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$ and $(\text{CH}_3)_3\text{N}$ are 854, 920, 950 and 970 respectively. Since these values increase from NH_3 to $(\text{CH}_3)_3\text{N}$, the basic strength of these amines increases in the order: $\text{NH}_3 < (\text{CH}_3)\text{NH}_2 < (\text{CH}_3)_2\text{NH} < (\text{CH}_3)_3\text{N}$.

Conjugate bases of HF, HCl, HBr and HI are F^- , Cl^- , Br^- and I^- respectively. PA values (in KJ/mole) of these conjugate bases are 1554, 1395, 1354 and 1315 respectively. Since these PA values decrease as $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$, the basicity of these conjugate bases also decreases in the same order: $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$. Due to the decrease in the basicity of conjugate bases, the acidity of conjugate acids of these bases (HF, HCl, HBr and HI are the conjugate acids of F^- , Cl^- , Br^- and I^-) increase in the order: $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$.

Conjugate bases of H_2O , H_2S and H_2Se are OH^- , SH^- and SeH^- respectively. PA values (in KJ/mole) of these conjugate bases are 1635, 1478 and 1420 respectively. Since these PA values decrease as $\text{OH}^- > \text{HS}^- > \text{HSe}^-$, the basicity of the conjugate bases also decreases in the same order: $\text{OH}^- > \text{SH}^- > \text{SeH}^-$. Due to the decrease in the basicity of conjugate bases, the acidity of conjugate acids of these bases (H_2O , H_2S and H_2Se are the conjugate acids of OH^- , SH^- and SeH^- respectively) increase in the order: $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se}$.

14. K_a Values of Acids and K_b Values of Bases

In aqueous solution, values of dissociation (or ionisation) constant of acids (K_a) are used to determine the relative strength of acids. The value of dissociation constant of an acid in aqueous solution is represented as K_a . K_a value of a weak acid (HA) in aqueous solution is given by equation (i) which is derived as follows. K_a is called **acidity constant**.



The equilibrium constant (K) for the above equilibrium is given by

$$K = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

or
$$\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = K \times [\text{H}_2\text{O}]$$

Now since $[\text{H}_2\text{O}] = \text{Constant}$,
$$\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = K \times \text{Constant} = K_a \quad \dots (i)$$

The value of K_a describes the relative acid strength of a weak acid. Equation (i) shows that larger is the value of acid dissociation constant (K_a) of an acid, higher

is the concentration of H_3O^+ ions and consequently stronger is the acid. For example since K_{CH_3COOH} value ($= 1.8 \times 10^{-5}$) for CH_3COOH is higher than K_{HCN} for HCN ($= 7.1 \times 10^{-10}$), CH_3COOH is stronger acid than HCN .

pK_a value is the negative logarithm of acidity constant (K_a), i.e. pK_a value is the negative logarithm of acidity constant (K_a), i.e.

$$pK_a = -\log K_a$$

This relation shows that:

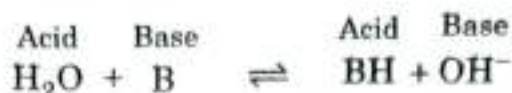
(a) Smaller is the value of pK_a , larger is the value of K_a and hence stronger is the acid. Thus stronger acids have larger K_a values and smaller pK_a values.

(b) Larger is the value of pK_a , smaller is the value of K_a and hence weaker is the acid. Thus weaker acids have smaller value of K_a and larger value of pK_a .

Table 3.3 Dissociation constants of some acids and bases at 25°C and their relative strength

Acids	Dissociation	K_a or K_b	Relative strength
Acids			
HCl	$HCl \rightleftharpoons H^+ + Cl^-$	Very large	Very strong
HNO ₃	$HNO_3 \rightleftharpoons H^+ + NO_3^-$	Very large	Very strong
H ₂ SO ₄	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	Large	Very strong
HSO ₄ ⁻	$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	1.3×10^{-2}	Strong
HF	$HF \rightleftharpoons H^+ + F^-$	6.7×10^{-4}	Weak
CH ₃ COOH	$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$	1.8×10^{-5}	Weak
H ₂ CO ₃ (H ₂ O + CO ₂)	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	4.4×10^{-7}	Weak
H ₂ S	$H_2S \rightleftharpoons H^+ + HS^-$	1.0×10^{-7}	Weak
NH ₄ ⁺	$NH_4^+ \rightleftharpoons H^+ + NH_3$	5.7×10^{-10}	Weak
HCO ₃ ⁻	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	4.7×10^{-11}	Weak
H ₂ O	$H_2O \rightleftharpoons H^+ + OH^-$	1.8×10^{-16}	Very weak
Bases			
NaOH	$NaOH \rightleftharpoons Na^+ + OH^-$	Very high	Very strong
KOH	$KOH \rightleftharpoons K^+ + OH^-$	Very high	Very strong
Ca(OH) ₂	$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$	High	Strong
NH ₄ OH	$NH_4OH \rightleftharpoons NH_4^+ + OH^-$	1.81×10^{-5}	Weak
CH ₃ NH ₂	$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.38×10^{-4}	Weak
C ₆ H ₅ NH ₂	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	4.70×10^{-10}	Very weak

The value of dissociation (or ionisation) constant of a base in aqueous solution is represented as K_b . K_b value of a base (B) is given by equation (ii) which is derived as follows:



The equilibrium constant (K) for the above equilibrium is given by:

$$K = \frac{[\text{BH}][\text{OH}^-]}{[\text{B}][\text{H}_2\text{O}]}$$

or
$$\frac{[\text{BH}][\text{OH}^-]}{[\text{B}]} = K \times [\text{H}_2\text{O}] = K \times \text{Constant}$$

or
$$\frac{[\text{BH}][\text{OH}^-]}{[\text{B}]} = K_b \quad \dots(ii)$$

This equation shows that larger is the value of base dissociation constant (K_b) of a base, higher is the concentration of OH^- ions and consequently strong is the base. For example since $K_{\text{C}_2\text{H}_5\text{OH}}$ value ($= 5.60 \times 10^{-4}$) is higher than $K_{\text{NH}_4\text{OH}}$ value ($= 1.81 \times 10^{-5}$), $\text{C}_2\text{H}_5\text{OH}$ is stronger base than NH_4OH . Stronger bases have lower $\text{p}K_b$ values and weaker bases have larger $\text{p}K_b$ values.

Values of dissociation constants (at 25°C) and relative strengths of some acids and bases are given in Table 3.3.

15. Resonance Effects

In addition to $-I$ and $+I$ effects, electron-withdrawing and electron-donating groups also have resonance effects. Electron-withdrawing resonance effect is represented as $-R$ effect. $-R$ effect increases the acidic strength of acids. In all the three nitrobenzoic acids, $-\text{NO}_2$ group which is an electron-withdrawing group has strong electron-withdrawing resonance effect ($-R$ effect) as well as electron-withdrawing inductive effect ($-I$ effects). Electron-donating resonance effect is represented as $+R$ effect. $+R$ effect decreases the acidic strength of acids. In all the three chlorobenzoic acids, $-\text{Cl}$ group which is an electron-donating group, has electron-donating resonance effect ($+R$ effect) as well as electron-withdrawing inductive effect ($-I$ effect).

How resonance concept affects the acidic strength of acids can be explained by considering the following examples:

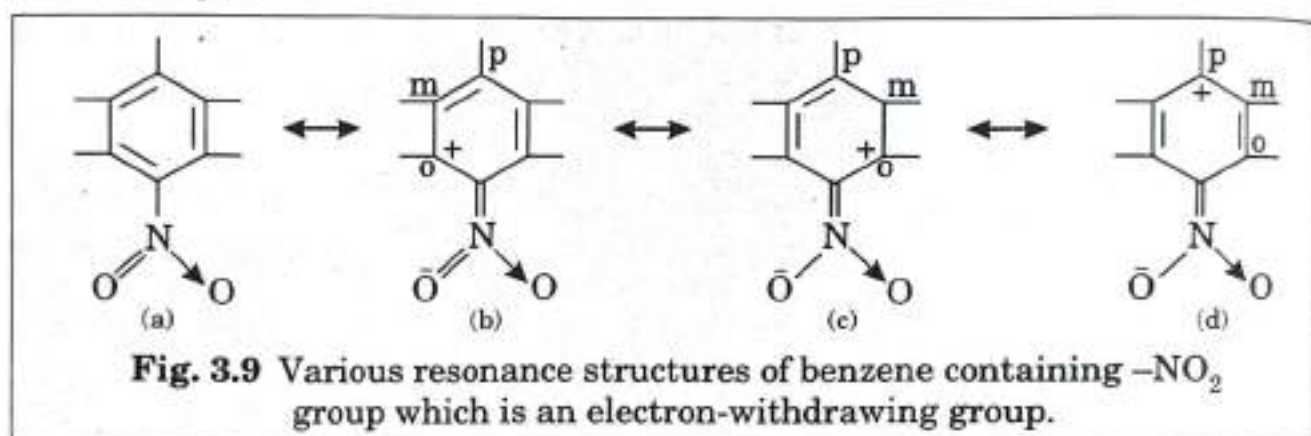
(i) Comparison of acidic strength of $\text{C}_6\text{H}_5\text{COOH}$ and nitrobenzoic acids

Nitrobenzoic acids have $-\text{COOH}$ and $-\text{NO}_2$ groups in the benzene ring. $-\text{NO}_2$ group present in these acids is an electron withdrawing group. This group may be present at any of the three positions *viz ortho* (*o*), *meta* (*m*) and *para* (*p*) in the benzene ring. Thus we have *o*-, *m*- and *p*-nitrobenzoic acids. It has been observed that $-\text{NO}_2$ group which is an electron-withdrawing group, placed at any of the three positions (*o*-, *m*- and *p*- positions) usually increases the acidic strength of nitrobenzoic acid, but $-\text{NO}_2$ group placed at *o*- and *p*-positions increases the acidic strength of the acids to a greater extent than when this group (i.e. $-\text{NO}_2$ group) is placed at *m*- position.

Further, when $-\text{NO}_2$ group is placed at *o*- position, the acid strength of *o*-nitrobenzoic acid increases to a greater extent than when $-\text{NO}_2$ group is placed at *p*-position (**ortho effect**), i.e. acid strength of *o*-nitrobenzoic acid is greater than that of *p*-nitrobenzoic acid. Thus the acid strength of nitrobenzoic acids *increases as* $m\text{-nitrobenzoic acid} < p\text{-nitrobenzoic acid} < o\text{-nitrobenzoic acid}$.

As a matter of fact, the acid strength of nitrobenzoic acids is much more than that explained above. The extra increase in acid strength is due to the **resonance effect** which has been explained below.

Various resonance structures of benzene containing $-\text{NO}_2$ group are given below in Fig. 3.9.

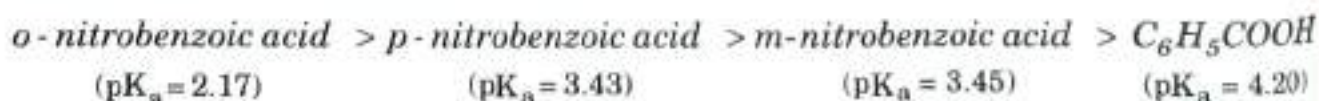


It may be seen from the resonance structures that *ortho* position (designated as *o*) (w.r.t. $-\text{NO}_2$ group) in structures (b) and (c) and *para* position (designated as *p*) in structure (d) are electron-deficient centres. Electron deficiency at *ortho* and *para* positions is caused by resonance effect. *Meta* position in all the four structures retains the original electron density. Therefore, the release of a proton (H^+) from COOH placed at *ortho* or *para* position w.r.t $-\text{NO}_2$ group would be easier. In other words, *o*- and *p*-nitrobenzoic acids would be stronger than $\text{C}_6\text{H}_5\text{COOH}$ itself and *m*-nitrobenzoic acid would be practically of the same strength as $\text{C}_6\text{H}_5\text{COOH}$.

It has been observed that *o*-nitrobenzoic acid is stronger than *p*-nitrobenzoic acid, although the electron deficiency caused by resonance effect at *o*- and *p*-positions is the same. Higher acidic strength of *o*-nitrobenzoic acid as compared to *p*-nitrobenzoic acid can be explained as follows:

In case of nitrobenzoic acids, electron-withdrawing inductive effect ($-\text{I}$ effect) as well as electron-withdrawing resonance effect ($-\text{R}$ effect) operate together. In case of *o*- and *p*-nitrobenzoic acids $-\text{R}$ effect is the same but $-\text{I}$ effect is different in these acids. This is because $-\text{I}$ effect of $-\text{NO}_2$ group decreases with the increase in the number of bonds separating $-\text{NO}_2$ group from COOH group. Hence *o*-nitrobenzoic acid is stronger than *p*-nitrobenzoic acid.

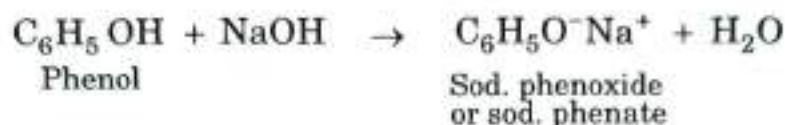
Above discussion shows that the relative order of acid strength of the three nitrobenzoic acids follows the order:



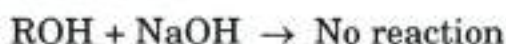
(ii) **Comparison of acidic strength of $\text{C}_6\text{H}_5\text{COOH}$ and its derivatives having electron-donating group at *o*-, *m*- and *p*-positions.** Benzoic acid

having an electron-donating group at *o*- and *p*-positions has lower acidic strength than C_6H_5COOH having an electron-donating group at *m*-position. This is due to resonance effect according to which electron density at *o*- and *p*-positions increases and hence the release of a proton from $COOH$ group is more difficult.

(iii) **Phenol (C_6H_5OH) is acidic but ethanol (C_2H_5OH) is neutral.** Phenols are acidic in nature since they turn blue litmus red and react with aqueous alkalis to form *metal phenoxides* or *metal phenates* ($C_6H_5O^-$)

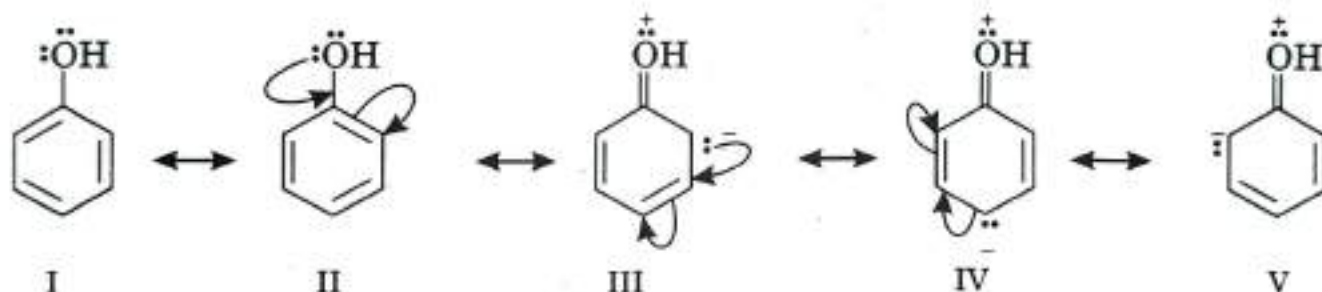


It may be noted that alcohols (ROH) neither turn blue litmus red nor react with NaOH. Thus alcohols are neutral.

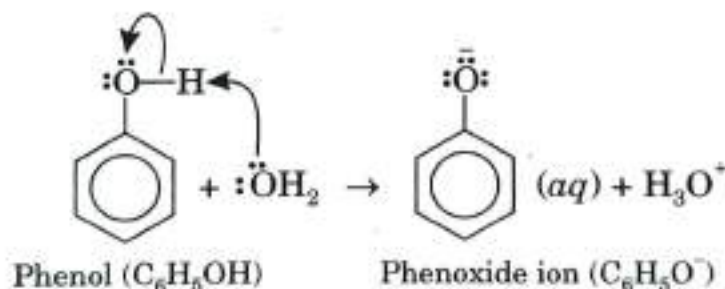


The fact that phenol is acidic and ethanol is neutral can be explained as follows on the basis of resonance stabilisation concept.

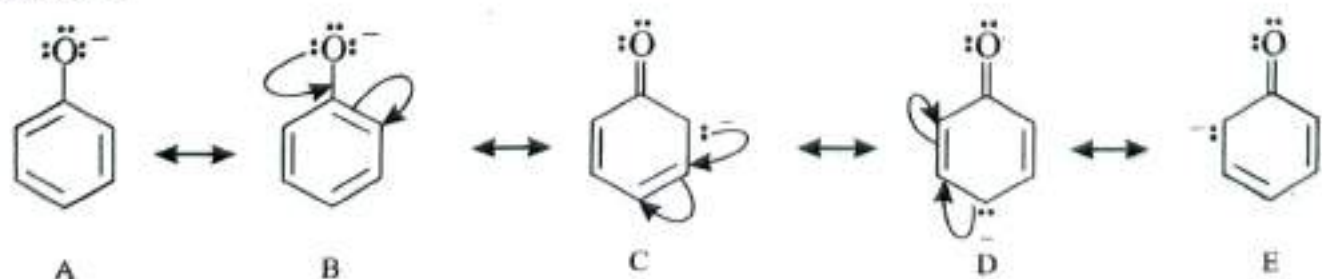
Phenol (C_6H_5OH) molecule is supposed to exist in the following resonance structures: I, II, III, IV and V.



It may be seen that O-atom of O-H bond in resonance structures III, IV and V has a partial positive charge. Due to the presence of positive charge, O-atom pulls the shared electron pair of O-H bond and thus the release of a proton is facilitated as shown below.

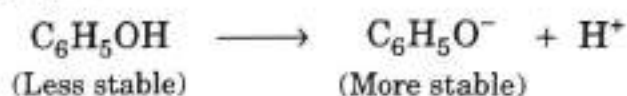


Phenoxide ion ($C_6H_5O^-$) also has the following resonance structures: A, B, C, D and E.



The occurrence of resonance in C_6H_5OH molecule and $C_6H_5O^-$ ion indicates that both these species acquire stability due to resonance, but $C_6H_5O^-$ ion acquires greater stability than C_6H_5OH molecule. This is because all the resonance structures of $C_6H_5O^-$ ion carry only negative charge which is localised. Thus resonance structures of $C_6H_5O^-$ ion do not have a separation of positive and negative charges. On the other hand, the resonance structures III, IV and V of C_6H_5OH molecule show that there is a separation of positive and negative charges in these structures. Thus resonance structures III, IV and V of C_6H_5OH molecule do not contribute much to the stability of C_6H_5OH molecule.

Due to the absence of charge separation in $C_6H_5O^-$ ion, this ion has greater stability than C_6H_5OH molecules, *i.e.* C_6H_5OH molecule is less stable than $C_6H_5O^-$ ion. Being less stable, C_6H_5OH molecule has great tendency to form more stable $C_6H_5O^-$ ion by releasing a proton.



The tendency of C_6H_5OH molecule to release a proton shows that C_6H_5OH has acidic character.

Ethanol (C_2H_5OH) loses a proton to form ethoxide ion ($C_2H_5O^-$). Since $C_2H_5O^-$ ion has only one structure, it has no resonance structures. Due to the absence of resonance structures, $C_2H_5O^-$ ion is less stable than its parental molecule, C_2H_5OH .



Being more stable, C_2H_5OH has negligible tendency to form less stable $C_2H_5O^-$ ion by releasing a proton. In other words C_2H_5OH is neutral. Neutral nature of C_2H_5OH is also evident from the facts that C_2H_5OH neither turns blue litmus red nor reacts with NaOH solution to form the salt.

Above discussion shows that C_6H_5OH has acidic character and C_2H_5OH is neutral because $C_6H_5O^-$ ion is stabilised by resonance but $C_2H_5O^-$ ion is not stabilised.

Points to Be Memorised

- (i) Stronger acid loses a proton (H^+) quite readily.
- (ii) Weak acid loses a proton with difficulty.
- (iii) Acid strength of an acid is determined by the readiness with which the acid donates a proton.
- (iv) Acid strength of an acid will be increased by any factor which increases the stability of the anion of the acid or which promotes the loss of a proton from the acid.
- (v) The group having greater electron-donating tendency has higher +I effect.
- (vi) The group having higher electron-donating power intensifies (increases) the negative charge on the anion obtained by removing a proton from an acid to a greater extent and hence makes the anion less stable.
- (vii) Some strong/weak acids and bases are given below.

Strong acids: HCl, HNO_3 , H_2SO_4

Weak acids: CH_3COOH , H_2CO_3 , H_3PO_4 , HF , NH_3

Strong bases: NaOH , KOH , $\text{Mg}(\text{OH})_2$

Weak bases: NH_4OH , $\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, $\text{Cu}(\text{OH})_2$

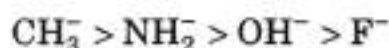
- (viii) In keeping with Arrhenius concept and Lowry concept, the relative strength of acids can be measured in terms of proton releasing ability of acids.

Relative Order of Acidic and Basic Strength of Some Species

Let us discuss the relative order of acidic/basic strength of the following molecules/ions.

1. Relative Order of Basic Strength (Basicity) of Conjugate Bases of CH_4 , NH_3 , H_2O and HF .

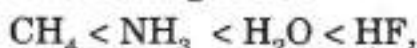
Conjugate bases of the given species are obtained by removing a proton (H^+) from the given species. Thus CH_3^- , NH_2^- , OH^- and F^- are conjugate bases of the given species. The basic strength of CH_3^- , NH_2^- , OH^- and F^- has been found in the following *decreasing order*.



————— Basic strength decreases —————>

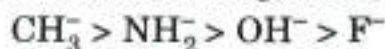
This decreasing order can be explained as follows:

(a) CH_4 , NH_3 , H_2O and HF are conjugate acids of CH_3^- , NH_2^- , OH^- and F^- conjugate bases. We know that in a given conjugate acid-base pair, if the acid is strong, its conjugate base would be weak. Similarly, if the base is strong, its conjugate acid would be weak. Now since the acidic strength of CH_4 , NH_3 , H_2O and HF (conjugate acids) is in the increasing order.



————— Acid strength increases —————>

the basic strength of CH_3^- , NH_2^- , OH^- and F^- which are conjugate bases of CH_4 , NH_3 , H_2O and HF would be in the decreasing order:



————— Basic strength decreases —————>

(b) It may be seen from the structures of the given bases that:

(i) in CH_3^- ion 3/4 of the volume of carbon atom carrying the negative charge is occupied by three H-atoms. Thus the negative charge on C-atom exists only on 1/4 volume of the carbon atom.

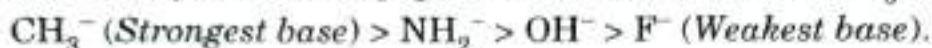
(ii) in NH_2^- ion 2/3 of the volume of N-atom carrying negative charge is occupied by two H-atoms. Thus the negative charge on N-atom exists only on 1/3 volume of N-atom.

(iii) in OH^- ion the negative charge on O-atom exists on more volume of O-atom

(iv) in F^- ion the negative charge on F^- atom exists on the whole volume of F-atom.

Thus the volume available to electron increases as we pass from CH_3^- to F^- ion. The increase in this volume increases the electron delocalisation from CH_3^- to

F^- ion. As the electron delocalisation increases, the electron density and hence the attraction for a proton decreases. The decrease in the attraction for a proton means that the basicity of these conjugate bases decreases from CH_3^- to F^- as shown below:



2. Relative Order of Basic Strength of the Hydrides of Group VA (15) Elements (NH_3 , PH_3 , AsH_3 , SbH_3 , BiH_3)

The hydrides formed by the elements of group 15 can be represented by the general formula, H_3M ($M = N, P, As, Sb, Bi$).

We know that the central atom, M in MH_3 hydrides has a lp of electrons in one of the four sp^3 hybrid orbitals. These molecules therefore have a tendency to donate the lp of electrons to the Lewis acids like H^+ , BF_3 , Ag^+ , Cu^+ , Cd^{2+} etc, i.e. MH_3 molecules show Lewis basic character due to the presence of lp of electrons on the central atom. As we move down the group from NH_3 to BiH_3 , the basic character of MH_3 molecules decreases as:



This order shows that NH_3 is distinctly basic and PH_3 is weaker base than NH_3 . AsH_3 , SbH_3 and BiH_3 do not show basic character.

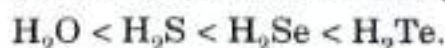
Explanation: Since the central atoms in MH_3 molecules are different, the decrease in basic character from NH_3 to BiH_3 can be explained on the basis of the size of the central atom. As the size of the central atom increases from N to Bi , the lp of electrons on the central atom occupies larger volume and hence the electron density due to lp of electrons round the central M -atom in MH_3 molecules to donate its lp of electrons to a Lewis acid also decreases. Thus the basic character decreases from NH_3 to BiH_3 ($NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$). NH_3 is the strongest base due to the smallest size of N -atom. Since P -atom is larger in size than N -atom, PH_3 is weaker base than NH_3 . Since the size of As , Sb and Bi is very large, the trihydrides of these elements (AsH_3 , SbH_3 and BiH_3) do not show basic character. These hydrides are neutral.

3. Relative Order of Acidic Strength of Hydrides of Group VIA (16) Elements (H_2O , H_2S , H_2Se , H_2Te)

The hydrides formed by the elements of group 16 can be represented by the formula, H_2M ($M = O, S, Se, Te$). M_2H molecule act as weak, diprotic or dibasic acids and thus dissociate in aqueous solution in two stages to give H^+ ions.



The acidic strength of H_2M molecules is in the following increasing order:



This increasing order can be explained as follows:

Explanation. As the atomic size increases down the group, the distance between the central atom (M) and hydrogen increases and the cleavage of $M-H$ bond ($M = O, S, Se, Te$ etc). becomes easier. As a result the tendency to release hydrogen as proton increases down the group (least in case of oxygen and maximum in case of tellurium).

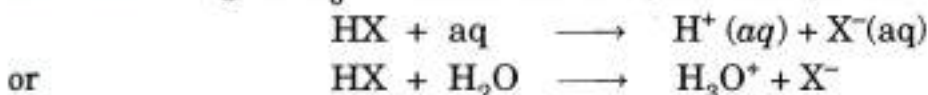
The increasing order of acidic strength is also supported by the following facts:

(i) As we move from H_2O to H_2Te , the magnitude of single bond dissociation energy decreases down the group ($H_2O = 464 \text{ KJ mol}^{-1}$, $H_2S = 339$, $H_2Se = 276$, $H_2Te = 247$). With the decrease in bond dissociation energy, the acidic strength of H_2M molecules increases.

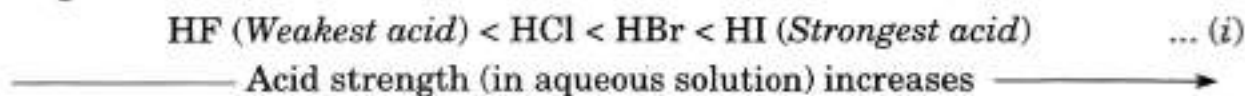
(ii) As the values of K_a^1 for H_2M molecules increases down the group (K_a^1 values for H_2M molecules are $H_2O = 1 \times 10^{-14}$, $H_2S = 1 \times 10^{-7}$, $H_2Se = 1.7 \times 10^{-4}$, $H_2Te = 2.3 \times 10^{-3}$), the acidic strength of H_2M molecules also increases in the same direction.

4. Relative Order of Acid Strength of Halogen Acids (HX) in Aqueous Solution (HF, HCl, HBr, HI)

In the gaseous state, hydrogen halides (HX) are covalent and hence do not show any acidic character. However, in **aqueous solution**, HX molecules undergo ionisation to give H_3O^+ and X^- ions and, therefore, behave as acids.



The acidic strength of hydrogen halides in aqueous solution follows the following increasing order:



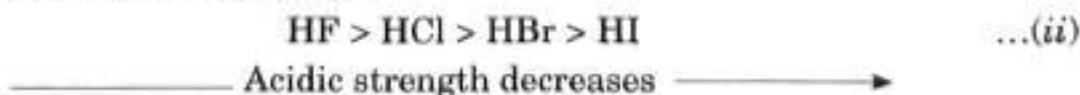
This order shows that HF is the weakest acid in aqueous solution and HI is the strongest acid in aqueous solution.

The above increasing order of acid strength of HX molecules in aqueous solution cannot be explained on the basis of electronegativity difference between X and H atoms as discussed below.

Since F atom has the highest value of electronegativity and I-atom has the minimum value, electronegativity difference between X and H atoms in HF, HCl, HBr and HI molecules decreases as:



Due to the decreasing order of electronegativity difference the percent ionic character in HF, HCl, HBr and HI molecules also decreases in the same order ($\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$). Since the percent ionic character decreases from HF to HI, acidic strength of HX molecules also decreases in the same order. Thus the acidic strength of HX molecules decreases as:



It may be seen that the order of acid strength shown at (i) above is the reverse of the order shown at (ii) which is based on electronegativity values of X and H atoms.

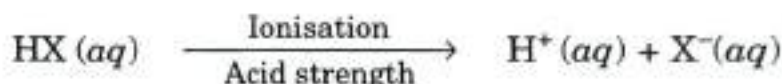
The increasing order of acid strength [shown at (i)] in aqueous solution can be explained as follows:

(i) *Explanation based on the dissociation energy of H-X bond.* Lesser is the magnitude of dissociation energy of H-X bond, more easily HX molecule will

dissociate in aqueous solution to give H_3O^+ and X^- ions and hence greater is the acid strength of HX molecule in aqueous solution. Now since bond dissociation energy (in KJ/mol) of H - X bond decreases from H - F to H - I (H - F = 574, H - Cl = 432, H - Br = 363 and H - I = 295), acid strength of halogen acids **increases** in the order:



(ii) *Explanation based on heats of ionisation (ΔH_I) of HX molecules in aqueous solution.* We have already stated that heat of ionisation of HX molecules in aqueous solution is the energy **released** in the ionisation of HX(aq) into $H^+(aq)$ into $H^+(aq)$ ions.



ΔH = Heat released = Heat of ionisation of HX (aq) = $-\Delta H_I$ of HX (aq)

Obviously larger is the value of ΔH_I (donot consider negative sign) for a given HX (aq) molecule, greater is the feasibility of ionisation of HX (aq) molecule into $H^+(aq)$ and $X^-(aq)$ ions and hence greater is the acid strength of HX (aq) molecule.

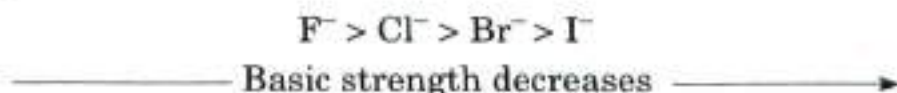
Now we know that the values of ΔH_I (in KJ mol⁻¹) for HF, HCl, HBr and HI molecules are:

HF	HCl	HBr	HI
-12	-59	-63	-57
————— ΔH_I values increase —————>			
(Do not consider negative sign)			

Since the value of ΔH_I for HF is the lowest, HF is the weakest acid. Further, since ΔH_I values increase from HF to HBr, the acid strength of HF, HCl and HBr is in the order: HF < HCl < HBr. We know that the order of acid strength of HX molecules in aqueous solution is HF < HCl < HBr < HI. The highest acid strength of HI in aqueous solution cannot be explained on the basis of its ΔH_I value. This discrepancy is explained on the basis of entropy changes (ΔS) accompanying the process of ionisation.

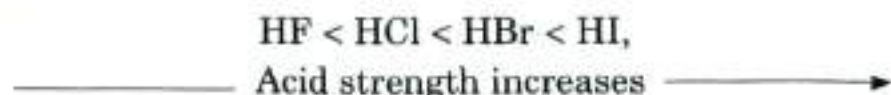
5. Relative Order of Basic Strength of Conjugate Bases of HF, HCl, HBr and HI (F^- , Cl^- , Br^- , I^-)

Conjugate bases of HF, HCl, HBr and HI are F^- , Cl^- , Br^- and I^- respectively, since these have been obtained by removing H^+ ion from HF, HCl, HBr and HI respectively. The basic strength of conjugate bases has been found in the following decreasing order:



This decreasing order can be explained as follows:

(a) *Explanation based a the relative order of acid strength of HF, HCl, HBr and HI.* HF, HCl, HBr and HI are the conjugate acids of F^- , Cl^- , Br^- and I^- . We know that since the acidic strength of HF, HCl, HBr and HI (conjugate acids) is in the *increasing order*

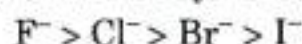


the basic strength of F^- , Cl^- , Br^- and I^- which are the conjugate bases of HF, HCl, HBr and HI should be in the *decreasing* (opposite) order



————— Basic strength decrease —————>

(b) *Explanation based on the size of halide ions.* We know that the size of F^- , Cl^- , Br^- and I^- ions increases on moving from F^- to I^- ($F^- < Cl^- < Br^- < I^-$). Due to the increase in size of X^- ions, the volume available to electron on X^- ion increases from F^- to I^- . The increase in the volume increases the delocalisation of the electron on X^- ion and hence the electron density on X^- ion decreases from F^- to I^- . As a result, the proton accepting power (*i.e.* basicity) of X^- ions decreases in the order:



————— Basicity decreases —————>

6. Relative Order of Acid Strength of Oxoacids of Chlorine ($HClO$, $HClO_2$, $HClO_3$, $HClO_4$)

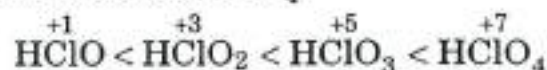
Oxoacids formed by Cl are $HClO$, $HClO_2$, $HClO_3$ and $HClO_4$. The acidic strength of these acids increases in the order:



————— Acidic strength increases —————>

This increasing order can be explained as follows:

In all the four oxoacids, since the electronegativity (EN) of the central atom (*i.e.* Cl atom) is the same, acidic strength of the acids does not depend on EN value of Cl-atom. Now since O.N. of Cl-atom in the given acids is different, acid strength of the acids depends on O.N. of Cl-atom. Acid strength increases with the increase of O.N. of Cl-atom. As O.N. of Cl-atom increases from +1 (in $HClO$) to +7 (in $HClO_4$), acid strength increases from $HClO$ to $HClO_4$.

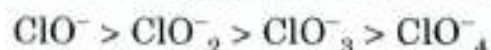


————— O.N. of Cl increases —————>

————— Acidic strength increases —————>

7. Relative Order of Basic Strength of Conjugate Bases of $HClO$, $HClO_2$, $HClO_3$ and $HClO_4$ (ClO^- , ClO_2^- , ClO_3^- , ClO_4^-)

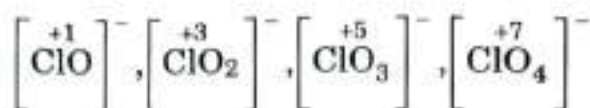
Conjugate bases of $HClO$, $HClO_2$, $HClO_3$ and $HClO_4$ are ClO^- , ClO_2^- , ClO_3^- and ClO_4^- , since these have been obtained by removing a proton (H^+) from the given acids. The basic strength of these conjugate bases **decreases** in the order:



————— Basic strength decreases —————>

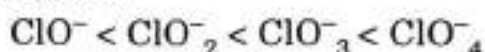
Explanation. This decreasing order can be explained as follows:

(a) *Explanation based on oxidation number (O.N.) of Cl-atom.* In the given oxoanions, since electronegativity (EN) of Cl-atom in all the four oxoanions remains the same, the basic strength of these anions decreases due to the increase in O.N. of Cl-atom from +1 in ClO^- to +7 in ClO_4^- . Thus:



_____ EN of Cl-atom remains the same _____ →
 _____ O.N. of Cl-atom increases from +1 to +7 _____ →
 _____ Basicity of oxoanions decreases _____ →

(b) *Explanation based on the stability of oxoanions.* We know that the stability of the given oxoanions increases as:



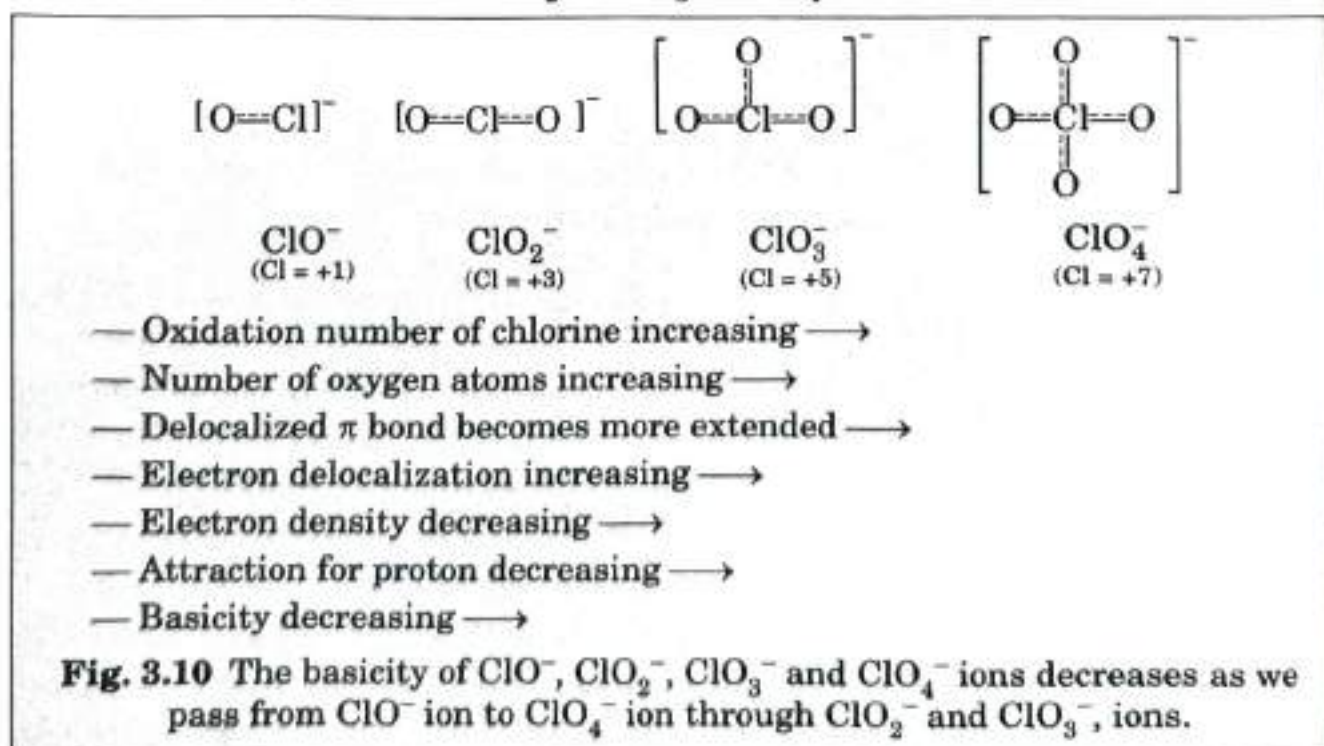
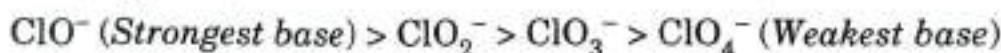
_____ Stability increases _____ →

Now since ClO^{-} ion is the least stable, it has the maximum tendency to accept a proton (H^{+}) to form its conjugate acid, HClO . Thus ClO^{-} is the strongest base. On the other hand, since ClO_4^{-} ion has the maximum stability (most stable), this ion has the minimum tendency to accept a proton to form its conjugate acid, HClO_4 . Thus ClO_4^{-} ion is the weakest base. Hence:



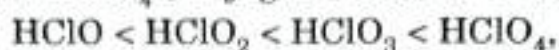
_____ Stability increases _____ →
 _____ Basic strength decreases _____ →

(c) *Explanation based on the electron density on ClO^{-} , ClO_2^{-} , ClO_3^{-} and ClO_4^{-} ions.* With the increase in the number of oxygen atoms in the conjugate bases, the delocalisation of the π bond becomes more and more extended. This results in decrease in electron density. Consequently, proton attraction and basicity also decrease (Fig. 3.10) in the order:



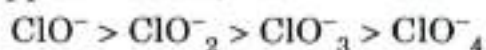
(d) *Explanation based on the relative order of acidic strength of HClO , HClO_2 , HClO_3 and HClO_4 .* HClO , HClO_2 , HClO_3 and HClO_4 are the conjugate acids of ClO^{-} ,

ClO_2^- , ClO_3^- and ClO_4^- (conjugate bases). We know that since the acidic strength of HClO , HClO_2 , HClO_3 and HClO_4 (conjugate acids) is in the increasing order:



————— Acidic strength increases —————>

the basic strength of ClO^- , ClO_2^- , ClO_3^- and ClO_4^- which are conjugate bases should be in the decreasing order (opposite order).



————— Basic strength decreases —————>

8. Relative order of Acid Strength of Hypohalous Acids (HClO , HBrO , HIO) and Perhalic Acids (HClO_4 , HBrO_4 , HIO_4).

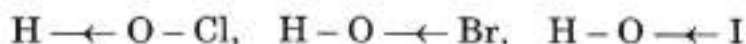
(a) Acid strength of hypohalous acids (HClO , HBrO and HIO) decreases in the order:



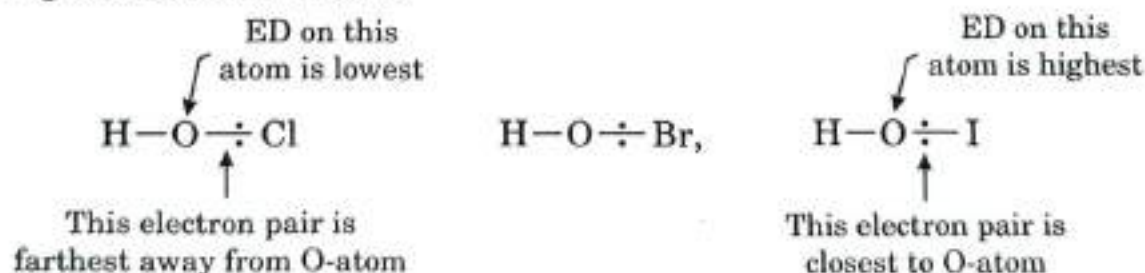
————— Acid strength decreases —————>

The acid strength of HClO , HBrO and HIO decreases with the decrease in electronegativity (EN) of halogen atom (central atom) from Cl to I as explained below.

The structure of HClO , HBrO and HIO molecules are $\text{H}-\text{O}-\text{Cl}$, $\text{H}-\text{O}-\text{Br}$ and $\text{H}-\text{O}-\text{I}$ respectively. Since O-atom is more electronegative than X-atom ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), this atom (i.e. O-atom) attracts the shared pair of electrons of $\text{O}-\text{X}$ bond towards itself as shown below.



Now since EN value of X-atom decreases from Cl to I ($\text{Cl} > \text{Br} > \text{I}$), the shared pair of electrons of $\text{O}-\text{X}$ bond moves close and closer towards O-atom and hence electron density on O-atom increases from HClO to HIO . In other words electron density (ED) on O-atom of HClO molecule is the lowest and that on O-atom of HIO is the highest as shown below.



Since ED on O-atom in $\text{H}-\text{O}-\text{Cl}$ is the lowest, this atom (i.e. O-atom) attracts the shared pair of electrons of $\text{H}-\text{O}$ bond toward itself *most strongly*. On the other hand, since ED on O-atom in $\text{H}-\text{O}-\text{I}$ is the highest, this atom (i.e. O-atom) attracts the shared pair of electrons of $\text{H}-\text{O}$ bond towards itself *least strongly*. Thus the tendency of O-atom to attract the shared pair of electrons in $\text{H}-\text{O}$ bond towards itself decreases from $\text{H}-\text{O}-\text{Cl}$ to $\text{H}-\text{O}-\text{I}$ as shown below.



As a result, $\text{O}-\text{H}$ bond breaks most readily in $\text{H}-\text{O}-\text{Cl}$ and least easily in $\text{H}-\text{O}-\text{I}$. In other words, we can say that as the electronegativity of halogen atom decreases from Cl to I, the possibility of the rupture of $\text{O}-\text{H}$ bond to give H^+ ions also decreases and hence the acid strength of HClO , HBrO and HIO decreases as :



————— Acid strength decreases —————>

(b) Acid strength of perhalic acids (HClO_4 , HBrO_4 and HIO_4) also decreases with the decrease in electronegativity from Cl to I.



————— Acid strength decreases —————>

The decrease in acid strength can be explained as follows:

As the electronegativity of halogen atom decreases from Cl to I, the tendency of XO_3 group in HXO_4 or $\text{O}_3\text{X}-\text{O}-\text{H}$ molecule to withdraw the electrons of $\text{O}-\text{H}$ bond towards itself decreases and hence acid strength of perhalic acids decreases in the same order, *i.e.*



————— Acid strength decreases —————>

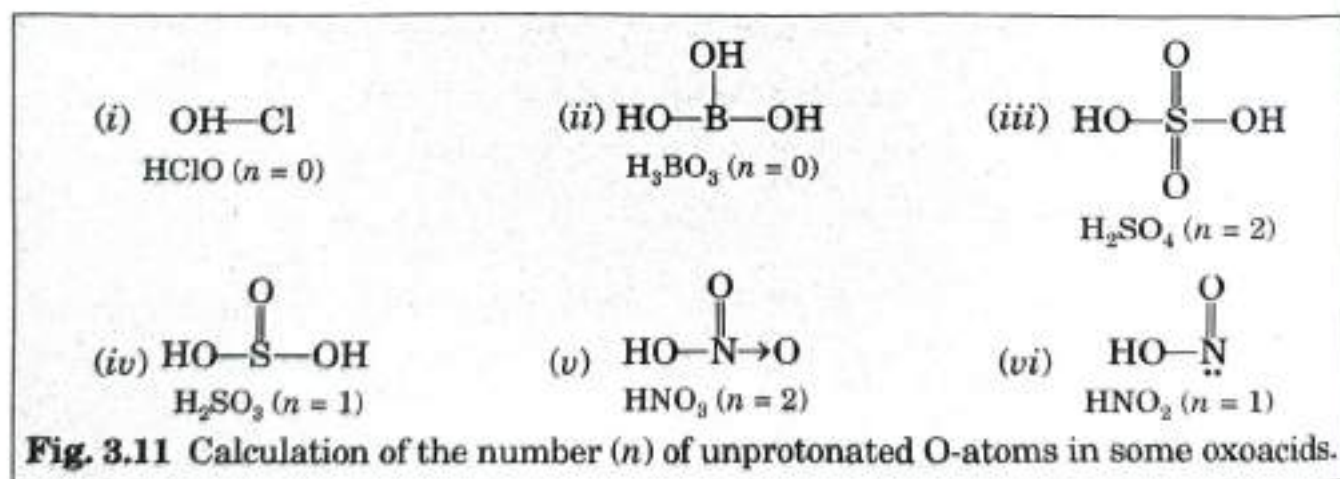
Pauling's Empirical Rule: Acidic Strength of Oxoacids

Pauling has introduced an empirical rule for estimating the acidic strength of oxoacids having the general formula, $\text{XO}_n(\text{OH})_m$ where n is the number of unprotonated O-atoms and m is the number of $-\text{OH}$ groups. pK_1 value of an oxoacid is approximately given by:

$$\text{pK}_1 = 7 - 5n$$

Thus if for an oxoacid $n = 0$, then $\text{pK}_1 = 7$ and hence the acid is weak. As the value of n increases, pK_1 becomes negative and the acid becomes strong. As the number of unprotonated O-atoms (n) increases, the overall inductive effect on the dissociation of the proton of $-\text{OH}$ group increases and hence acid strength increases.

Examples. The number of unprotonated O-atoms (n) in some oxoacids has been calculated in Fig. 3.11.

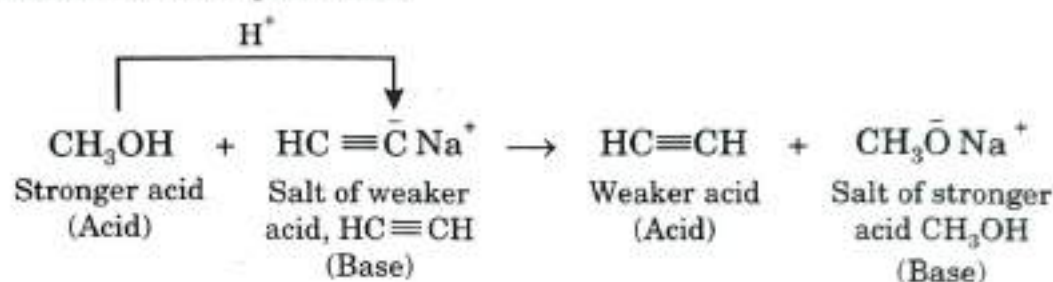


Since $n = 0$ for HClO and H_3BO_3 , both these acids are very weak acids. Since the value of n for H_2SO_4 ($n = 2$) is greater than that for H_2SO_3 ($n = 1$), the former is a stronger acid than the latter. Similarly, since HNO_3 ($n = 2$) has greater value of n than HNO_2 ($n = 1$), the former is a stronger acid than the latter.

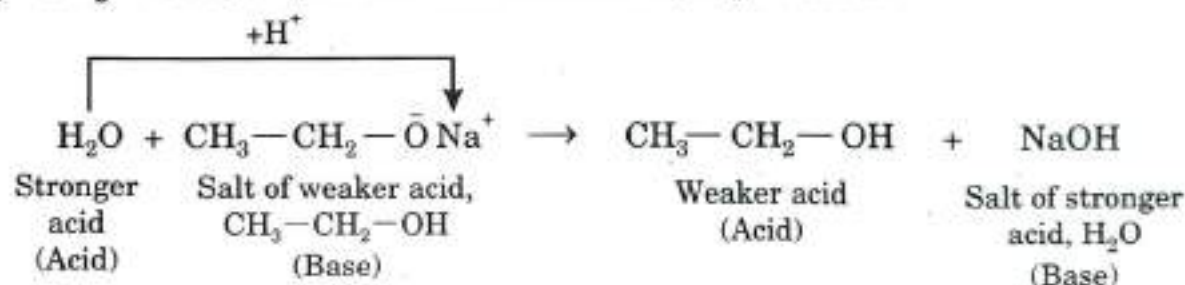
Reaction Between a Stronger Acid and the Salt of a Weaker Acid

If we have two acids one of which is a stronger acid and the other is a weaker acid, then the reaction between the stronger acid and the salt of the weaker acid produces the weaker acid and salt of the stronger acid. For example:

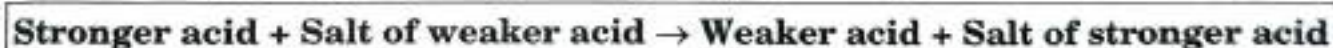
(i) Since CH_3OH is a stronger acid than $\text{HC} \equiv \text{CH}$, in the reaction between CH_3OH (stronger acid) and $\text{HC} \equiv \text{CNa}^+$ (salt of weaker acid, $\text{HC} \equiv \text{CH}$), stronger acid (i.e. CH_3OH) donates a proton (H^+) to the salt and weaker acid, $\text{HC} \equiv \text{CH}$ (i.e. parental acid of salt) is produced.



(ii) Since H_2O is a stronger acid than $\text{CH}_3-\text{CH}_2-\text{OH}$, in the reaction between H_2O (stronger acid) and $\text{CH}_3-\text{CH}_2-\text{O}^-\text{Na}^+$ (salt of weaker acid, $\text{CH}_3-\text{CH}_2-\text{OH}$), the stronger acid (i.e. H_2O) donates a proton (H^+) to the salt and weaker acid, $\text{CH}_3-\text{CH}_2-\text{OH}$ (i.e. parental acid of the salt) is produced.

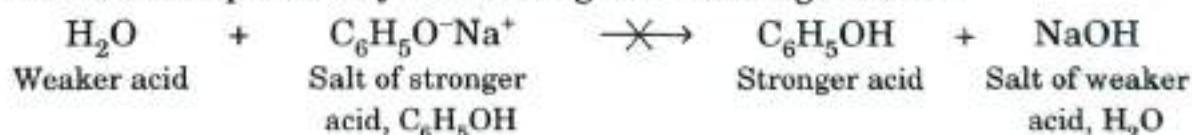


In general :



Reaction Between a Weaker Acid and the Salt of a Stronger Acid

The reaction between a weaker acid and the salt of a stronger acid can not take place. This can be explained by considering the following reaction.



In the above reaction, H_2O is a weaker acid than $\text{C}_6\text{H}_5\text{OH}$. This reaction will not take place, since H_2O , being a weaker acid, is not able to donate a proton (H^+) to $\text{C}_6\text{H}_5\text{O}^-\text{Na}^+$ to form $\text{C}_6\text{H}_5\text{OH}$ (strong acid)

In general, the following reaction cannot take place.



Advantages of Bronsted - Lowry concept over Arrhenius Concept.

(i) According to Bronsted-Lowry concept, not only molecules but even the anions can also act as acids or bases. For example in the following reaction CO_3^{2-} ion acts as a base



(ii) It can explain the basic character of the substances like Na_2CO_3 , NH_3 etc. (which do not contain OH^- group and hence were not bases according to Arrhenius definition) on the basis that they are proton acceptors.

(iii) It can explain the acid-base reactions in the non-aqueous medium or even in the absence of a solvent For example in the following acid-base reaction no aqueous solution is required.



Limitation of Bronsted-Lowry Concept

Although Bronsted-Lowry concept has a wider scope than the Arrhenius concept but it has some limitations, e.g.,

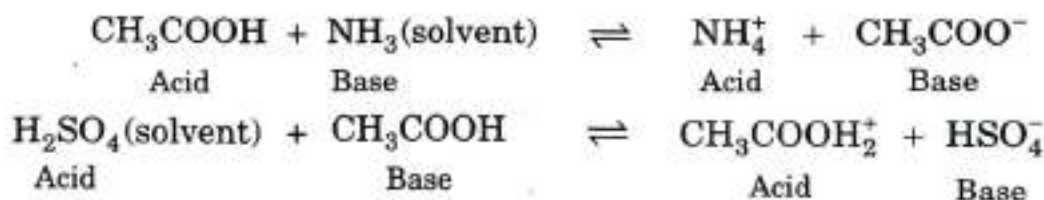
(i) It cannot explain the reactions between acidic oxides like CO_2 , SO_2 , SO_3 etc. and the basic oxides like CaO , BaO , MgO etc. which take place even in the absence of the solvent, e.g.,



Obviously, there is no proton transfer involved in this reaction.

(ii) Substances like BF_3 , AlCl_3 etc., do not have any hydrogen and hence cannot give a proton but are known to behave as acids.

(iii) A given substance may behave as an acid in one solvent and may behave as a base in some other solvent. For example CH_3COOH behaves as an acid in liquid NH_3 and as a base in H_2SO_4 solvent as is evident from the following equilibria.

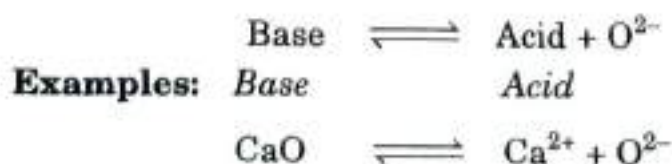


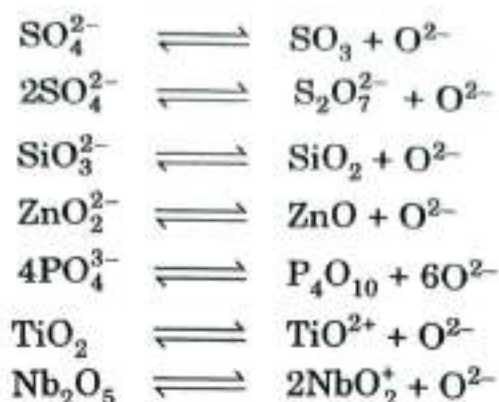
The dual behavior of CH_3COOH cannot be explained by Bronsted-Lowry Concept.

IV. Lux-Flood Concept

Definition

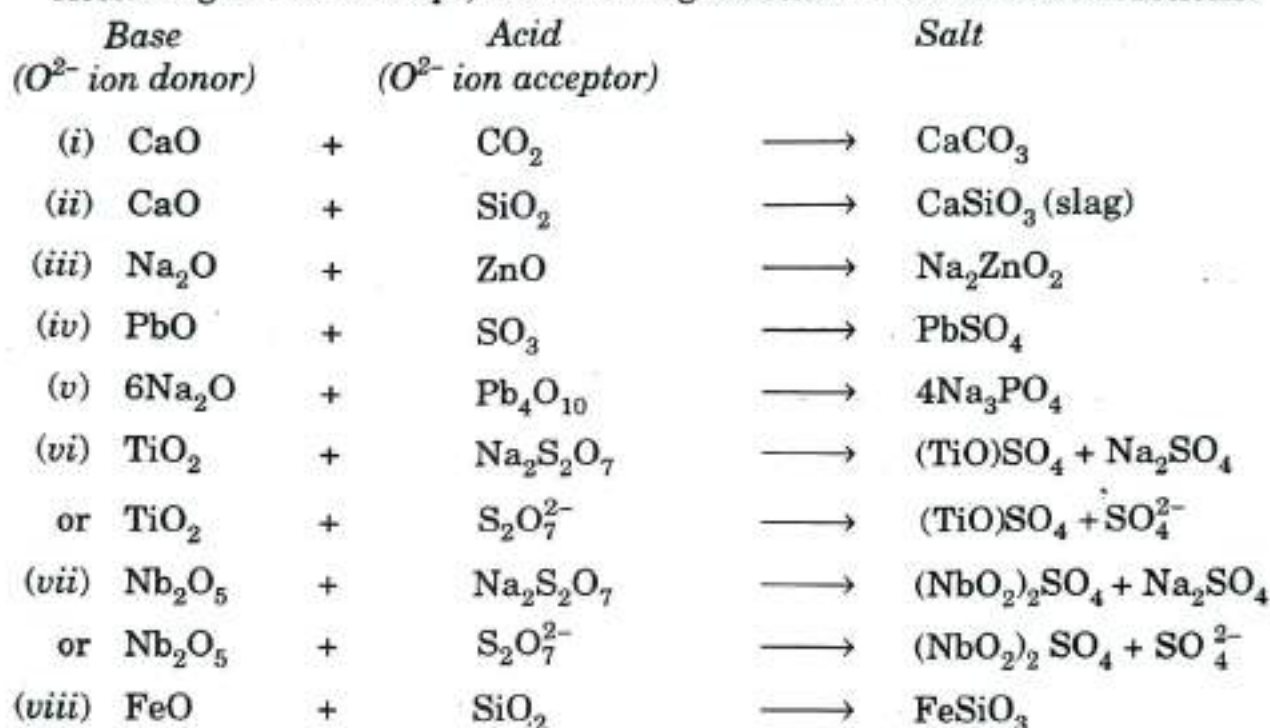
This concept was proposed by Lux (1939) and extended by Flood (1947). This concept explains the formation of salts by the combination of acids and bases in the absence of a solvent. The formation of salt involves the transfer of an oxide ion (O^{2-}) from the base to the acid. The compound which loses (donates) an O^{2-} ion acts as a base and the species which accepts the O^{2-} ion acts as an acid. In other words *base is O^{2-} ion donor and the acid is O^{2-} ion acceptor.* Thus:



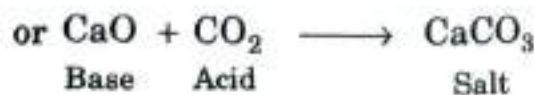
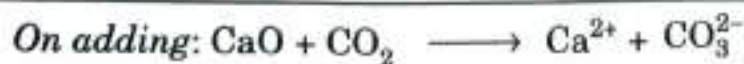
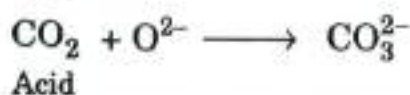


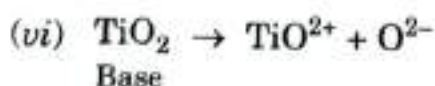
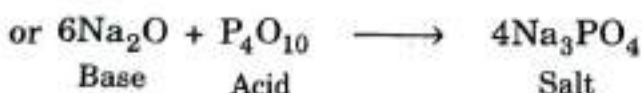
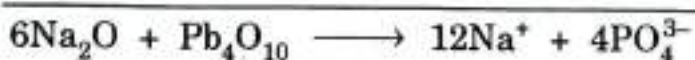
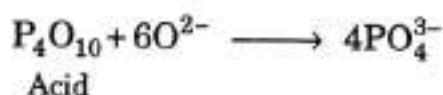
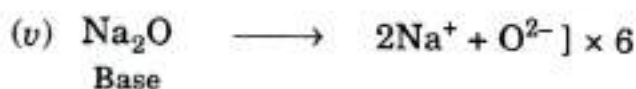
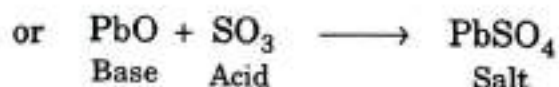
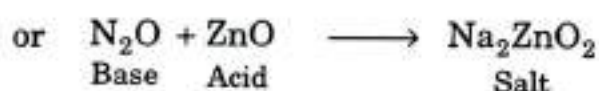
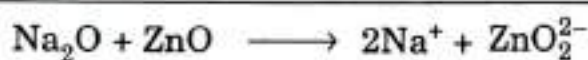
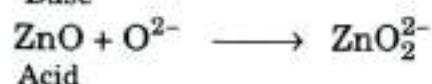
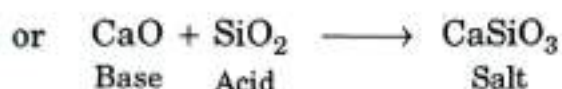
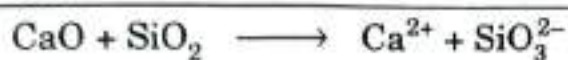
Acid-Base Reactions.

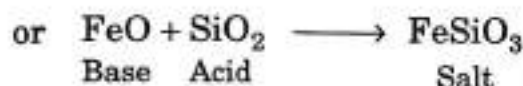
According to Lux concept, the following reactions are acid-base reactions.



In the above acid-base reactions the oxides *viz* CaO, Na_2O , PbO, TiO_2 , Nb_2O_5 and FeO act as bases, since these oxides donate O^{2-} ion to CO_2 , SiO_2 , ZnO, SO_3 , Pb_4O_{10} and $\text{Na}_2\text{S}_2\text{O}_7$ (or $\text{S}_2\text{O}_7^{2-}$) which act as acids because these species accept O^{2-} ion given by bases. The transfer of O^{2-} ion from the base to the acid in each of the above reactions has been explained below:



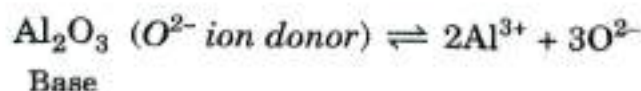
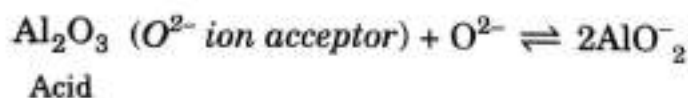
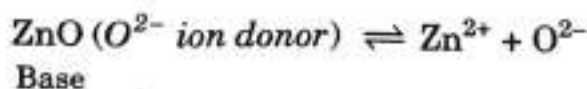
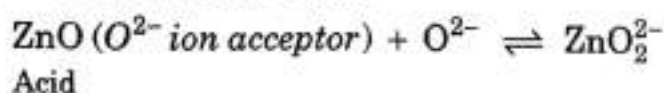




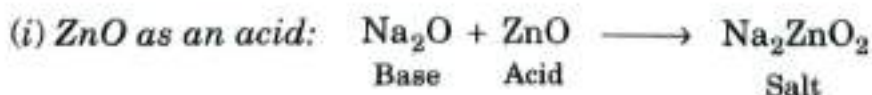
It is obvious from the above Lux acid-base reactions that these reactions are *non-protonic acid-base reactions*.

Amphoteric Behavior of ZnO and Al₂O₃.

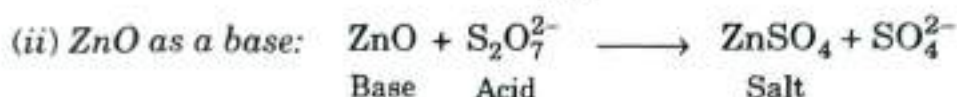
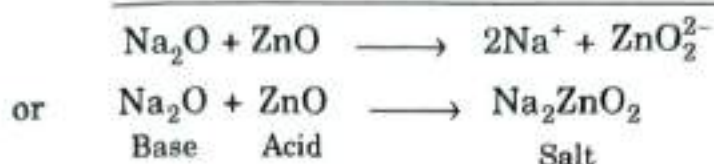
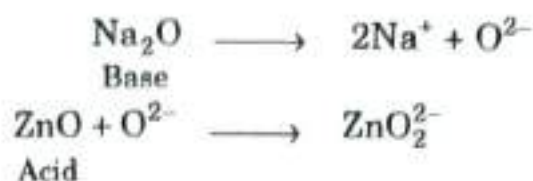
According to Lux concept ZnO and Al₂O₃ both show amphoteric behavior, since these oxides behave as acids by accepting an O²⁻ ion and behave as bases by donating an O²⁻ ion as shown below:



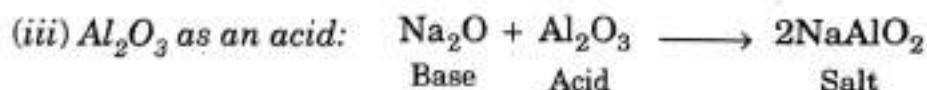
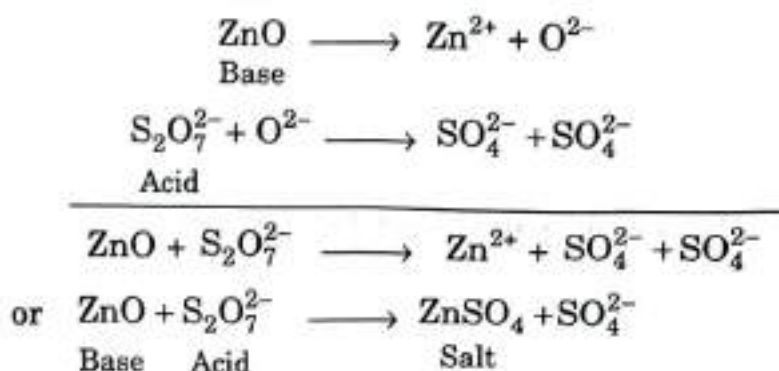
Amphoteric behaviour of ZnO and Al₂O₃ is evident from the following acid-base reactions.



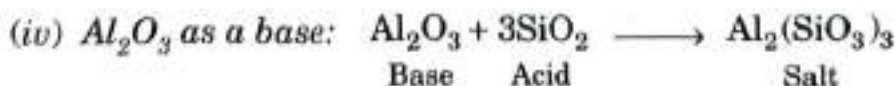
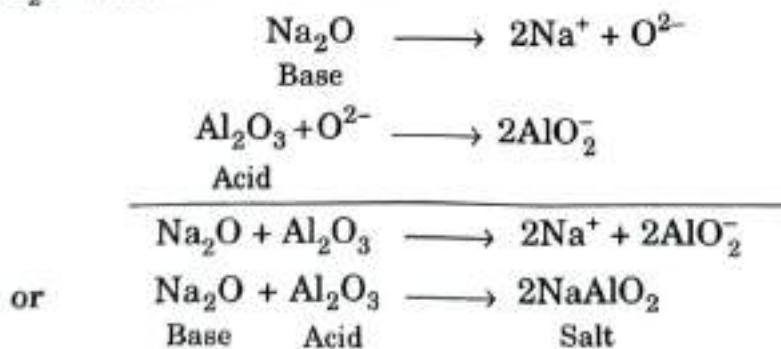
In this reaction ZnO behaves as an acid because it accepts an O²⁻ ion donated by Na₂O which acts as a base.



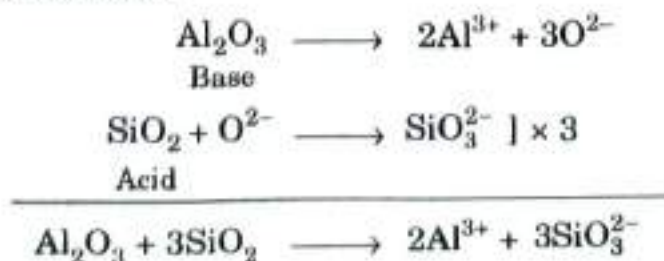
In this reaction ZnO behaves as a base since it donates an O^{2-} ion to $\text{S}_2\text{O}_7^{2-}$ ion which acts as an acid.

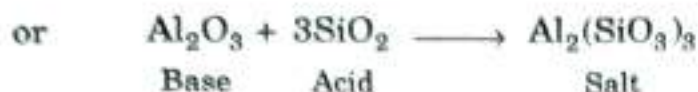


In this reaction Al_2O_3 behaves as an acid since it accepts an O^{2-} ion donated by Na_2O which acts as a base.



In this reaction Al_2O_3 behaves as a base because it donates an O^{2-} ion to SiO_2 which acts as an acid.



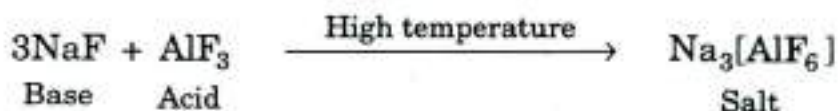


Lux Concept is Also Covered by Lewis Concept

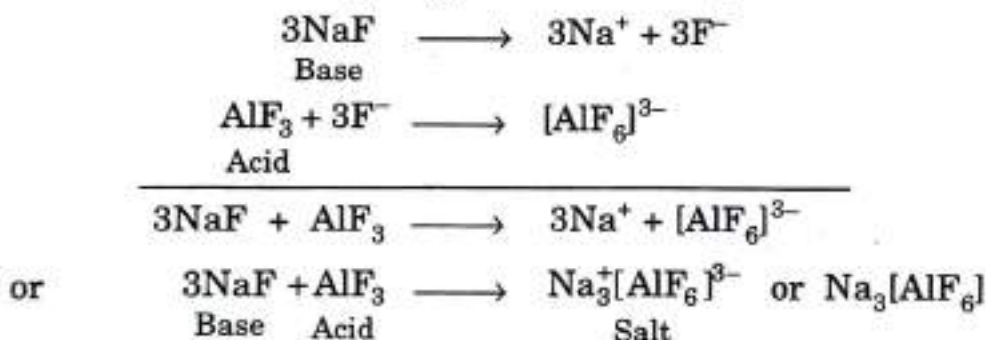
According to Lewis concept, an acid is an electron pair acceptor and a base is an electron pair donor. According to Lux concept, an acid is O^{2-} ion acceptor and a base is O^{2-} ion donor. Thus, according to Lux concept, an electron pair is shifted from the base to the acid *via* O^{2-} ion. In other words we say that Lux concept is also covered by Lewis concept.

Extension of Lux-Flood Concept

Lux-Flood concept has been extended and according to this extension, the substance that gives up (loses) an anion like halide (X^-), sulphide (S^{2-}) etc is called a base and the substance that gains the anion is called an acid. For example.



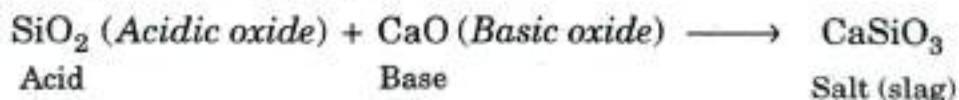
The formation of $\text{Na}_3[\text{AlF}_6]$ (salt) can be explained as follows:



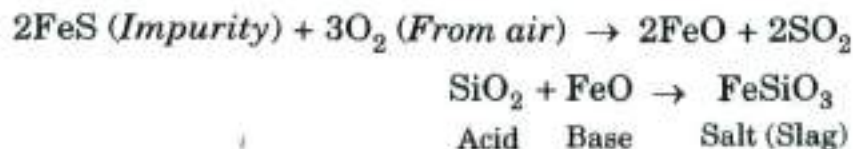
Applications of Lux Concept

Lux definition of acids and bases is applicable in ceramics and metallurgy. For example:

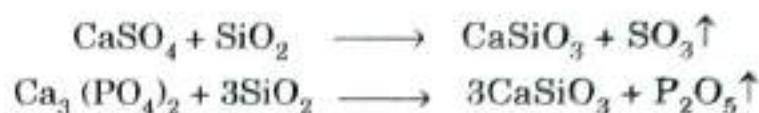
(i) In the metallurgy of iron, SiO_2 (acidic oxide) present in iron ore is removed by adding CaO (basic oxide) in blast furnace.



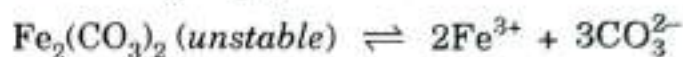
(ii) In the metallurgy of Cu from its sulphide ore, the impurity of FeS is removed by mixing the ore with SiO_2 and heating it in reverberatory furnace in the supply of air.



(iii) The basic nature of clay (CaSO_4) and phosphates [$\text{Ca}_3(\text{PO}_4)_2$] is revealed from their reactions with SiO_2 where more volatile oxides are removed and the oxide ion (O^{2-}), left behind, is transferred to SiO_2 .



(iv) The oxide ion (O^{2-}) acceptor nature of metal ions has been used to explain the decomposition (instability) of metal carbonates and sulphates. For example the instability (decomposition) of $\text{Fe}_2(\text{CO}_3)_3$ as shown below



indicates that Fe^{3+} ion is strongly acidic and hence rapidly accepts O^{2-} ion from CO_3^{2-} ion to form $\text{Fe}_2(\text{CO}_3)_3$. Thus $\text{Fe}_2(\text{CO}_3)_3$ is unstable.

Acidity Scale

On the basis of Lux-Flood concept, an acidity scale has been prepared. In this scale, each oxide is given acidity parameter value (α). The acidity parameter of an acid and a base is represented as α_A and α_B respectively. The difference, ($\alpha_A - \alpha_B$) has been found to be equal to $\sqrt{\Delta H}$ where ΔH is the enthalpy change in the reaction (heat of reaction) between the acid and the base.

$$\alpha_A - \alpha_B = \sqrt{\Delta H}$$

Example. Since the heat of reaction (ΔH) involving the combination of CaO (base) and SiO_2 (acid) is -86 KJ/mole , $\alpha_A - \alpha_B = \sqrt{85} = 9$ units (approximate value). The values of α for some oxides are given below:

Basic oxides: $\text{Na}_2\text{O} = -12.5$, $\text{Rb}_2\text{O} = -15.0$, $\text{Cs}_2\text{O} = -15.2$, $\text{SrO} = -9.4$.

Amphoteric oxides: $\text{H}_2\text{O} = 0.0$, $\text{ZnO} = -3.2$, $\text{Al}_2\text{O}_3 = -2.0$

Acidic oxides: $\text{SiO}_2 = 0.9$, $\text{N}_2\text{O}_5 = 9.3$, $\text{P}_4\text{O}_{10} = 7.5$, $\text{SO}_2 = 7.1$, $\text{SO}_3 = 10.5$, $\text{MoO}_3 = 5.2$, $\text{Mn}_2\text{O}_7 = 9.6$, $\text{Cl}_2\text{O}_7 = 11.5$

From the values given above the following points may be noted:

(i) The value of α of basic oxides is negative. More negative is the value of α , more is the basic character of the oxide. Thus Cs_2O is the most basic oxide.

(ii) The value of α of amphoteric oxides is close to zero. For example α for H_2O , ZnO and Al_2O_3 is as $\text{H}_2\text{O} = 0.0$, $\text{ZnO} = -3.2$ and $\text{Al}_2\text{O}_3 = -2.0$.

(iii) The value of α for acidic oxides is positive. Higher is the positive value of α , more is the acidic character of the oxide. Thus Cl_2O_7 is the most acidic oxide.

V. Solvent-System (Auto-ionisation) Concept

This concept was put forth by Franklin. This concept is based on the dissociation of solvents.

Auto-ionisation of Solvents.

Before learning the definition of acids and bases on the basis of solvent system concept we should have a knowledge of the nature of ions obtained by the auto-ionisation (self ionisation or dissociation) of some protonic and non-protonic solvents as shown below:

Protonic solvents:

<i>Solvent</i>		<i>Solvent cation</i> (Acid ion)		<i>Solvent anion</i> (Base ion)
2H ₂ O	⇌	H ₃ O ⁺	+	OH ⁻
2NH ₃	⇌	NH ₄ ⁺	+	NH ₂ ⁻
2CH ₃ COOH	⇌	CH ₃ COOH ⁺ ₂	+	CH ₃ COO ⁻
2H ₂ SO ₄	⇌	H ₃ SO ₄ ⁺	+	HSO ₄ ⁻

Non-protonic solvents:

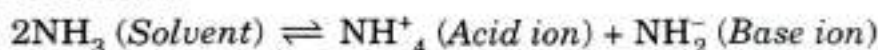
<i>Solvent</i>		<i>Solvent cation</i> (Acid ion)		<i>Solvent anion</i> (Base ion)
2BrF ₃	⇌	BrF ₄ ⁺	+	BrF ₂ ⁻
2N ₂ O ₄	⇌	NO ⁺ (Nitrosyl ion)	+	NO ₃ ⁻
COCl ₂	⇌	COCl ⁺	+	Cl ⁻
POCl ₃	⇌	POCl ₂ ⁺	+	Cl ⁻
2SO ₂	⇌	SO ²⁺ (Thionyl ion)	+	SO ₃ ²⁻

Definition of Acids and Bases

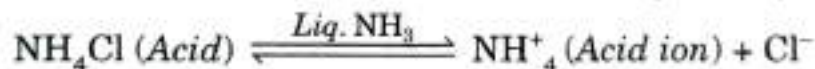
According to solvent system concept, an acid is a substance which, by dissolution in the solvent, gives the solvent cation (acid ion) obtained by the auto-ionisation of the solvent itself. A base is a substance which, by dissolution in the solvent, gives the solvent anion (base ion) obtained by the ionisation of the solvent itself.

In general we can say that any species that gives solvent cations (acid ions) in a given solvent behaves as an acid in that solvent. Similarly, any species that gives solvent anions (base ions) in a given solvent behaves as a base in that solvent.

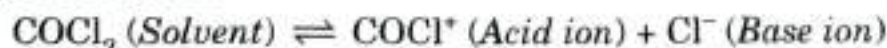
Examples (i) We know that liq. NH₃, on ionisation, gives NH₄⁺ (acid ion) and NH₂⁻ (base ion) ions.



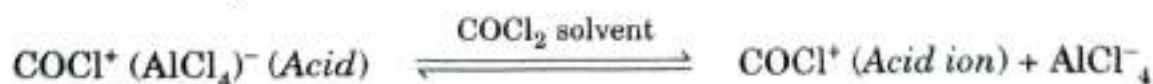
Hence, since NH₄Cl gives NH₄⁺ ion (acid ion) and KNH₂ gives NH₂⁻ ion (base ion) in NH₃ solvent, these salts behave as acid and base respectively in this solvent.



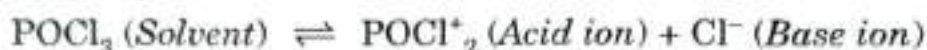
(ii) We know that COCl₂ solvent, on ionisation, gives COCl⁺ (acid ion) and Cl⁻ (base ion) ions



Now since COCl⁺ (AlCl₄)⁻ gives COCl⁺ ion (acid ion) and CaCl₂ gives Cl⁻ ion (base ion) in COCl₂ solvent, COCl⁺ (AlCl₄)⁻ behaves as an acid and CaCl₂ behaves as a base in COCl₂ solvent.



(iii) We know that POCl_3 solvent, on ionisation, gives POCl_2^+ (acid ion) and Cl^- (base ion)



Now since FeCl_3 gives POCl_2^+ ion (acid ion) in POCl_3 solvent, this salt behaves as an acid in this solvent.



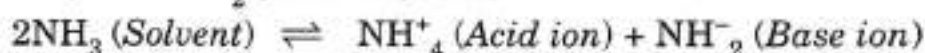
Since $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$ gives Cl^- ion (base ion) in POCl_3 solvent, this salt behaves as a base in this solvent.



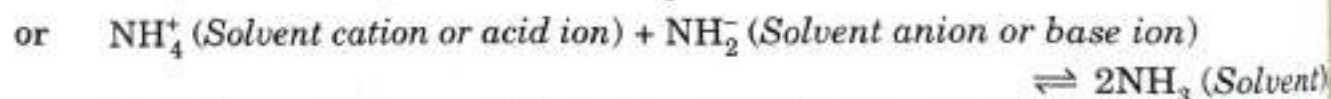
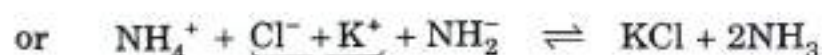
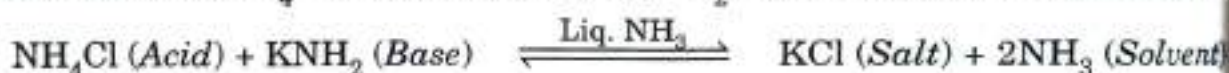
Acid-Base Neutralisation Reactions According to Solvent System Concept

According to solvent system concept of acids and bases, acid-base neutralisation reaction between an acid and a base is the combination of solvent cation (acid ion) and solvent anion (base ion) to form the solvent. This is clear from the following examples:

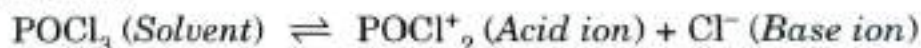
Examples (i) We know that, on self ionisation, liq. NH_3 (solvent) gives NH_4^+ (acid ion) and NH_2^- (base ion) ions.



Further in this solvent, since NH_4Cl gives NH_4^+ ion (acid ion) and KNH_2 gives NH_2^- ion (base ion), the acid-base reaction between NH_4Cl (acid) and KNH_2 (base) is the combination of NH_4^+ (solvent cation) and NH_2^- (solvent anion) as shown below.



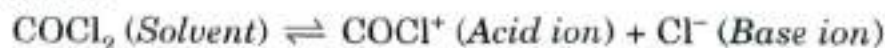
(ii) We know that, on self ionisation POCl_3 (solvent) gives POCl_2^+ (acid ion) and Cl^- (base ion) ions.



Further in this solvent, since FeCl_3 gives POCl_2^+ ion (acid ion) and $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$ gives Cl^- ion (base ion), the acid-base reaction between FeCl_3 (acid) and $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$ (base) is the combination of POCl_2^+ (solvent cation) and Cl^- (solvent anion) to form POCl_3 (solvent)



(iii) We know that, on self-ionisation, COCl_2 (solvent) gives COCl^+ (acid ion) and Cl^- (base ion) ions



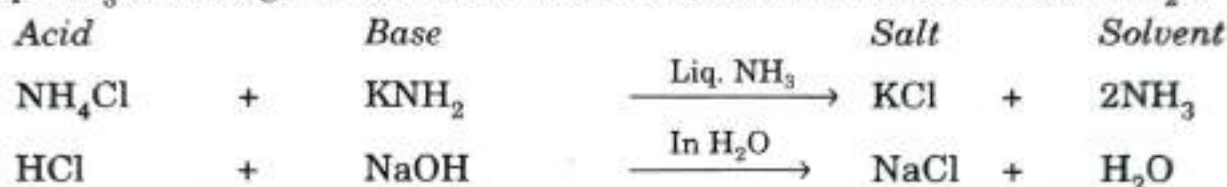
Further, since in this solvent, $\text{COCl}(\text{AlCl}_4)^-$ gives COCl^+ ion (acid ion) and CaCl_2 gives Cl^- ion (base ion) the acid-base reaction between $\text{COCl}^+(\text{AlCl}_4)^-$ (acid)

and CaCl_2 (base) is the combination of COCl^+ (solvent cation) and Cl^- (solvent anion) to form COCl_2 (solvent)

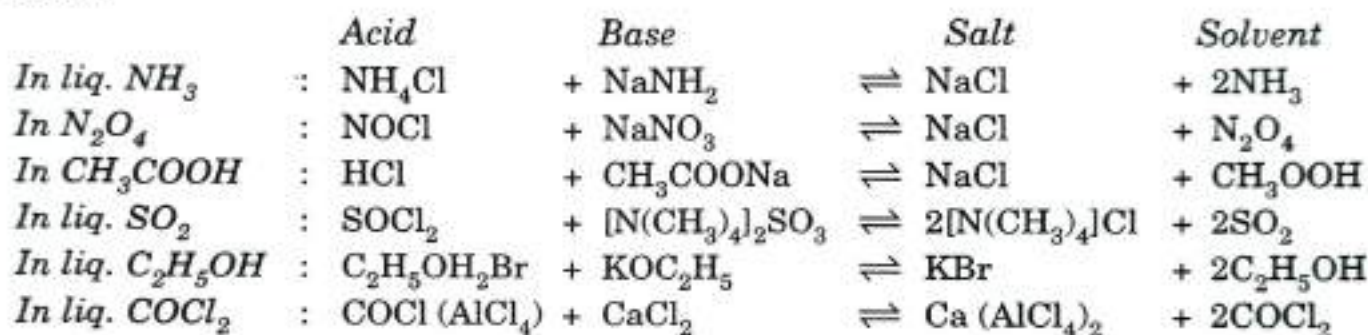


Thus we see that acid-base neutralisation reaction between an acid and a base proceeds in the direction opposite to that of the auto-ionisation of the solvent.

The acid-base neutralisation reaction between NH_4Cl (acid) and KNH_2 (base) in liq. NH_3 is analogous to that between HCl (acid) and NaOH (base) in H_2O

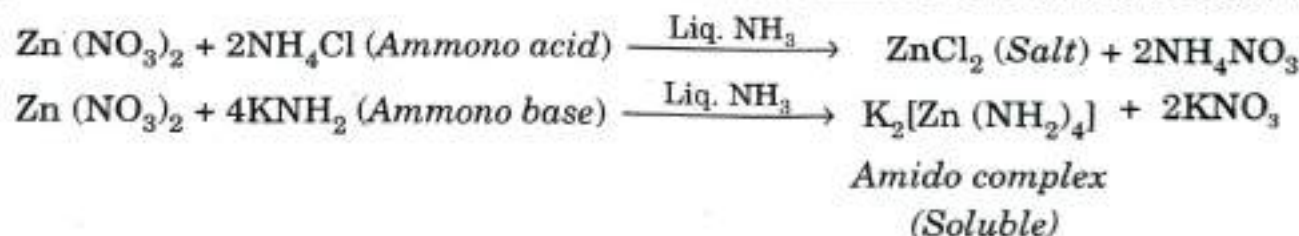


Newtralisation reactions in some protonic and non-protonic solvens are given below:



Amphoteric Behaviour of $\text{Zn(NO}_3)_2$ in liq. NH_3

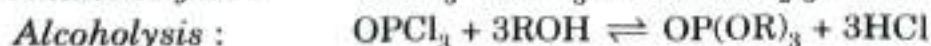
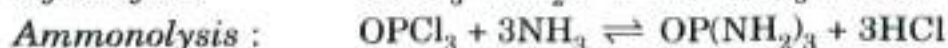
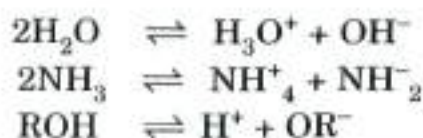
$\text{Zn(NO}_3)_2$ shows amphoteric behavior in liq. NH_3 , since in this solvent, this compound can react with ammonio acid as well as with ammonio base as shown below:



Utility of the Concept

(i) The solvent-system concept can be used to explain the acid-base reaction occurring in aqueous and non-aqueous solvents (protonic and non-protonic solvents).

(ii) The hydrolysis of non-metal halides (e.g. POCl_3) is analogous to the ammonolysis and alcoholysis reactions of these halides. In these reactions Cl^- ion of the halide is replaced by the base ion obtained by the ionisation of the solvent. For example:

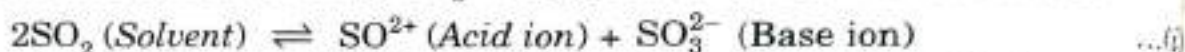


Limitations of the Concept

(i) Acid-base reaction is dictated by the mode of ionisation of the solvent and the nature of the ions obtained by the auto-ionisation of the solvent.

(ii) Acid-base reactions taking place in the absence of solvent cannot be explained by solvent-system concept.

(iii) The self-ionisation of liq. SO_2 is supposed to take place as follows:



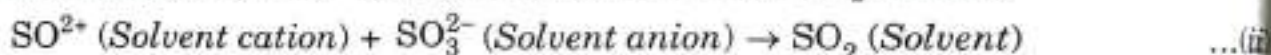
Thus since SOCl_2 gives SO^{2+} ion (acid ion) in liq. SO_2 , this salt behaves as an acid in liq. SO_2



Also since Cs_2SO_3 gives SO_3^{2-} ion (base ion) in liq. SO_2 , this salt behaves as a base in liq. SO_2



Since SOCl_2 is an acid and Cs_2SO_3 is a base in liq. SO_2 , the neutralisation reaction between SO_2Cl_2 (acid) and Cs_2SO_3 (base) is the combination between SO^{2+} (solvent cation) and SO_3^{2-} (solvent anion) to produce SO_2 solvent



The above reaction does occur between SOCl_2 (acid) and Cs_2SO_3 (base). Since the self-ionisation of liq. SO_2 as represented by equation (i) has not been established at all, the occurrence of acid-base reaction (ii) cannot be explained on the basis of self ionisation of SO_2 .

VI. Lewis Concept : Electron Pair Acceptor-Donor Concept

In the early 1930s, G.N. Lewis defined an acid as a molecule or an ion that can accept an electron pair from some other substance and a base as a molecule or an ion which can donate an electron pair (lone pair of electrons) to some other substance. *In other words, a Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor.*

Since Lewis acid is an electron pair acceptor, it is an electron-deficient species. Similarly since Lewis base is an electron pair donor, it is an electron rich species.

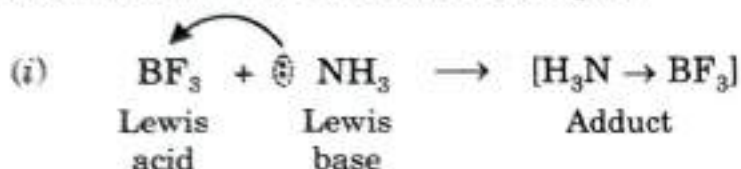
Since a Lewis acid loves to accept the electron pair (s), it is also called an *electrophilic* (electro = electron, philic = lover) *reagent* or simply *electrophile*. Similarly, since a Lewis base loves to donate the electron pair (s) to a nucleus, in fact to a positively charged ion, it is a *nucleus lover* or *nucleus-seeker* and hence is also called *nucleophilic* (nucleo = nucleus, philic = lover) *reagent* or simply *nucleophile*.

Lewis acid should contain one or more vacant orbitals into which electron pair (s) donated by the Lewis base can be accommodated.

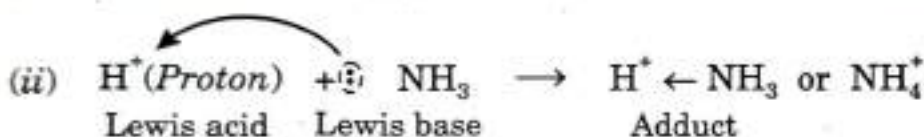
An acid qualifying Lewis concept is called Lewis acid and a base qualifying Lewis concept is termed as Lewis base.

Neutralisation Reaction According to Lewis Concept

According to Lewis concept of acids and bases, the neutralisation reaction is that in which a Lewis acid reacts with a Lewis base and forms a compound which is called an *adduct* or *complex compound*. This compound contains (Lewis base \rightarrow Lewis acid) coordinate bond. For example:



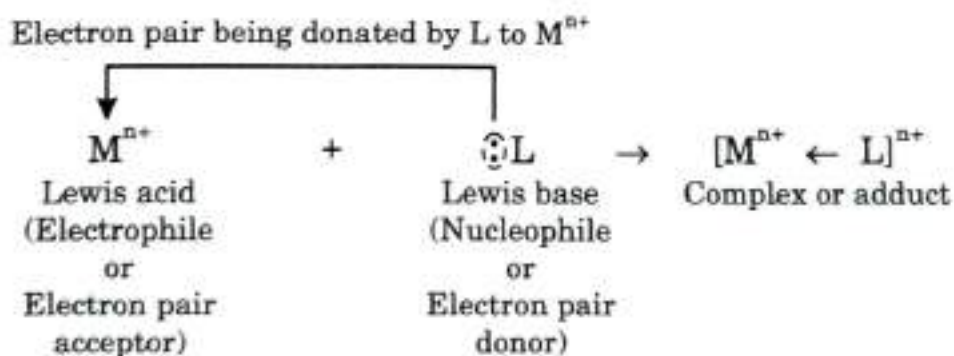
(Lewis base \rightarrow Lewis acid) coordinate bond results by the overlap of the filled orbital on the Lewis base with the vacant orbital on the Lewis acid.



Evidently in the above reaction proton (H^+) accepts one electron pair from :NH_3 molecule and is, therefore, an acid, whereas :NH_3 molecule which donates an electron pair, is a base. The adduct is NH_4^+ ion.

Lewis Acids and Lewis Bases in Coordination Chemistry

In coordination chemistry, the central metal ion, M^{n+} is regarded as a Lewis acid (*i.e.* electrophile), since it accepts an electron pair while the ligand, L is regarded as Lewis base (*i.e.* nucleophile), since it donates an electron pair. The compound formed by the combination of metal cation (M^{n+}) and ligand (L) is called a *complex* or an *adduct*.



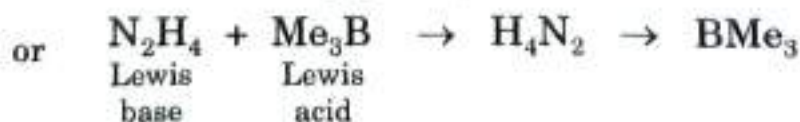
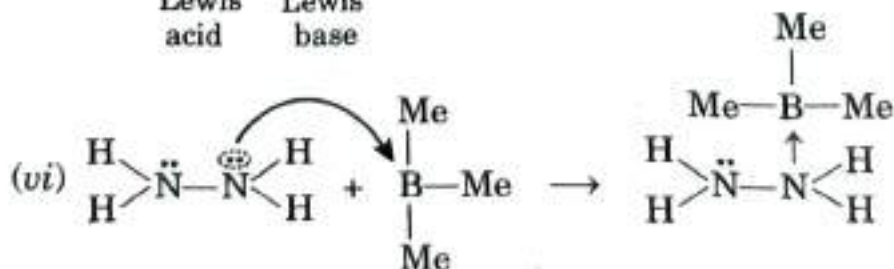
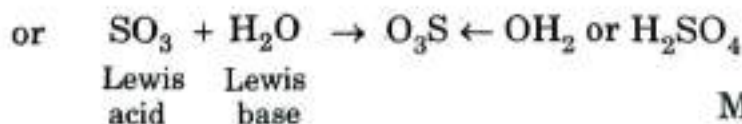
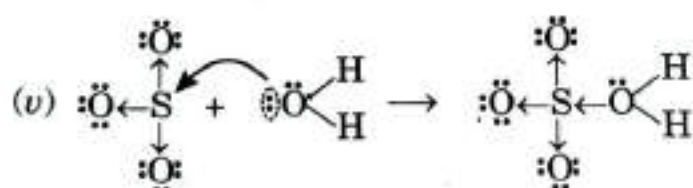
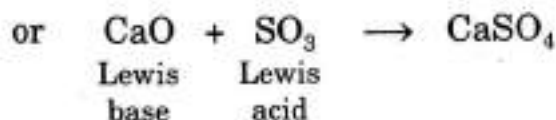
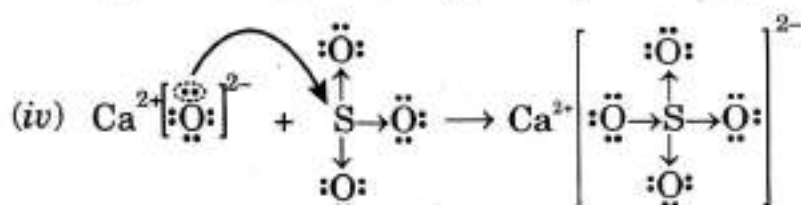
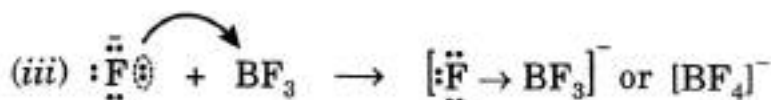
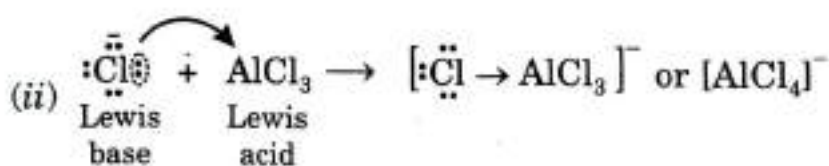
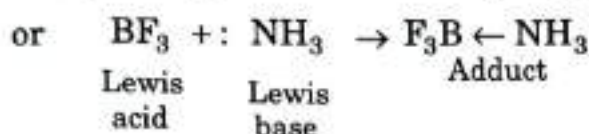
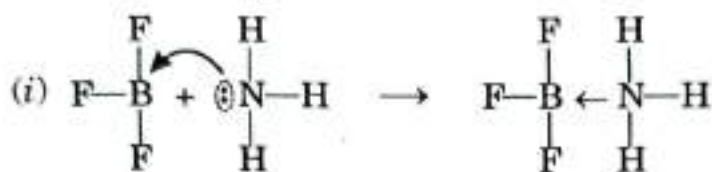
M^{n+} and L are linked together by a coordinate covalent bond from L to M^{n+} ($\text{M}^{n+} \leftarrow L$ bond). Thus the reaction between a metallic cation, M^{n+} and a ligand, L shown above can be considered as an acid-base reaction according to Lewis concept.

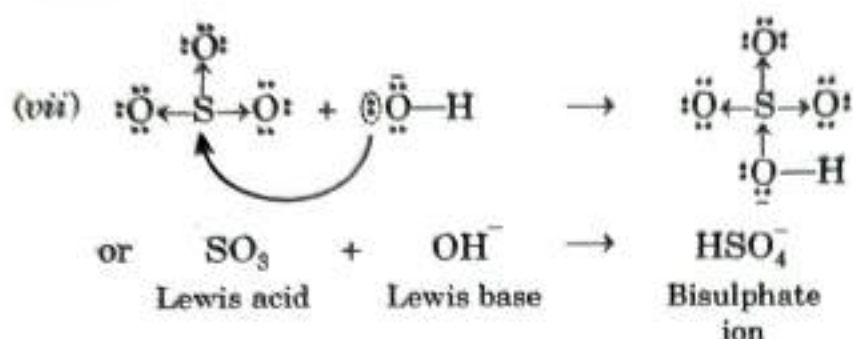
The metallic cation (Lewis acid) must have at least one vacant orbital in its valence-shell in which it can accommodate the electron pair donated by the ligand (Lewis base) and the ligand should have at least one lone pair of electrons so that it may be donated to the metallic cation.

Classification of Lewis Acids

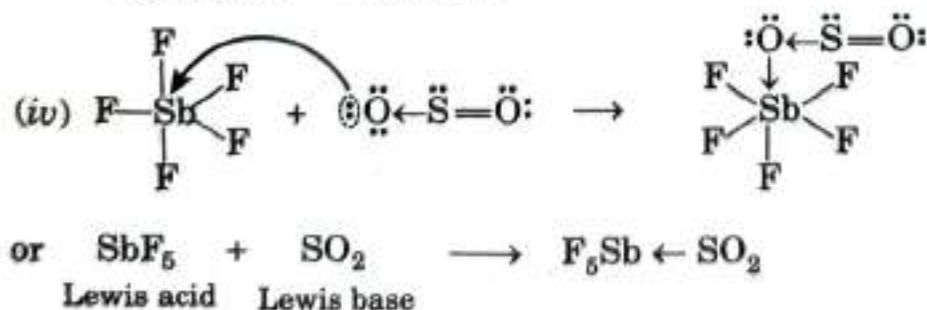
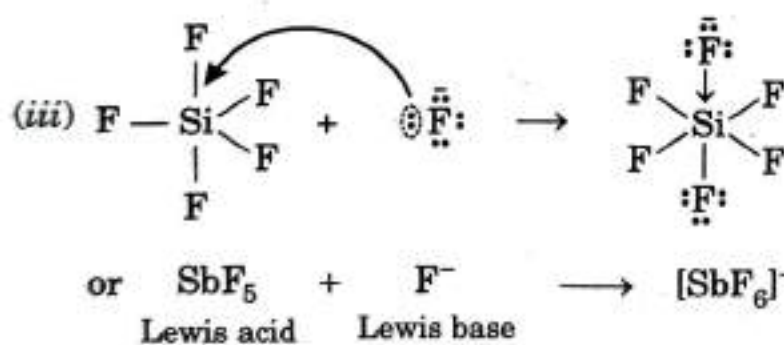
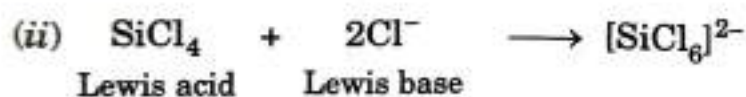
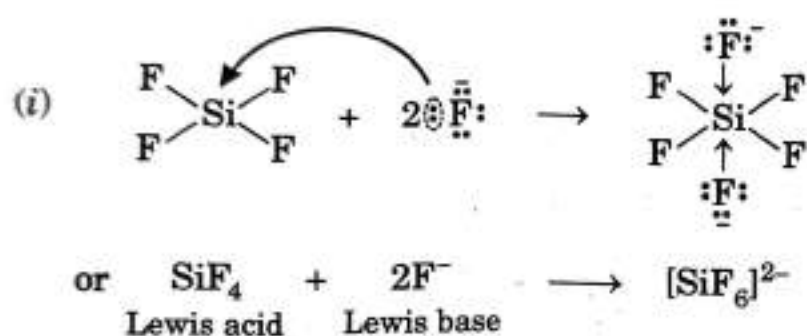
Any Lewis acid must contain at least one empty orbital in the valence shell of one of its atoms to accept an electron pair from a Lewis base. Lewis acids may be classified as:

1. Molecules containing a central atom with incomplete octet. Molecules having a central atom with incomplete octet are electron deficient and hence can accept a *lp* of electrons donated by Lewis base. Thus such molecules act as Lewis acids. Examples of such molecules are BF_3 , BCl_3 , AlCl_3 , Me_3B , SO_3 etc.

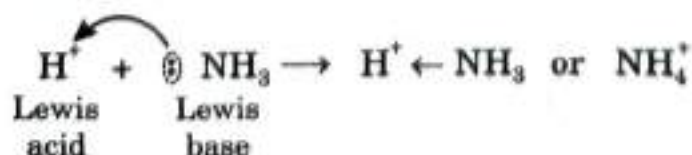




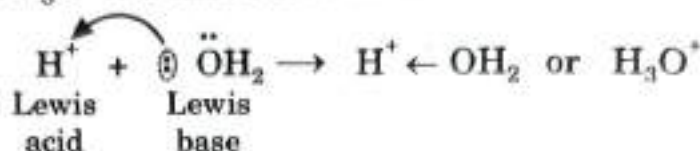
2. Molecules containing central atom with empty d-orbitals: The empty d-orbitals of the central atom in molecules like SiX_4 ($\text{X} = \text{F}, \text{Cl}$ etc.), SbF_5 etc. can accommodate electron pair (s) donated by Lewis base like halide ion ($\text{F}^{\ominus}, \text{Cl}^{\ominus}$ etc.), SO_2 molecule etc. Examples are given below:



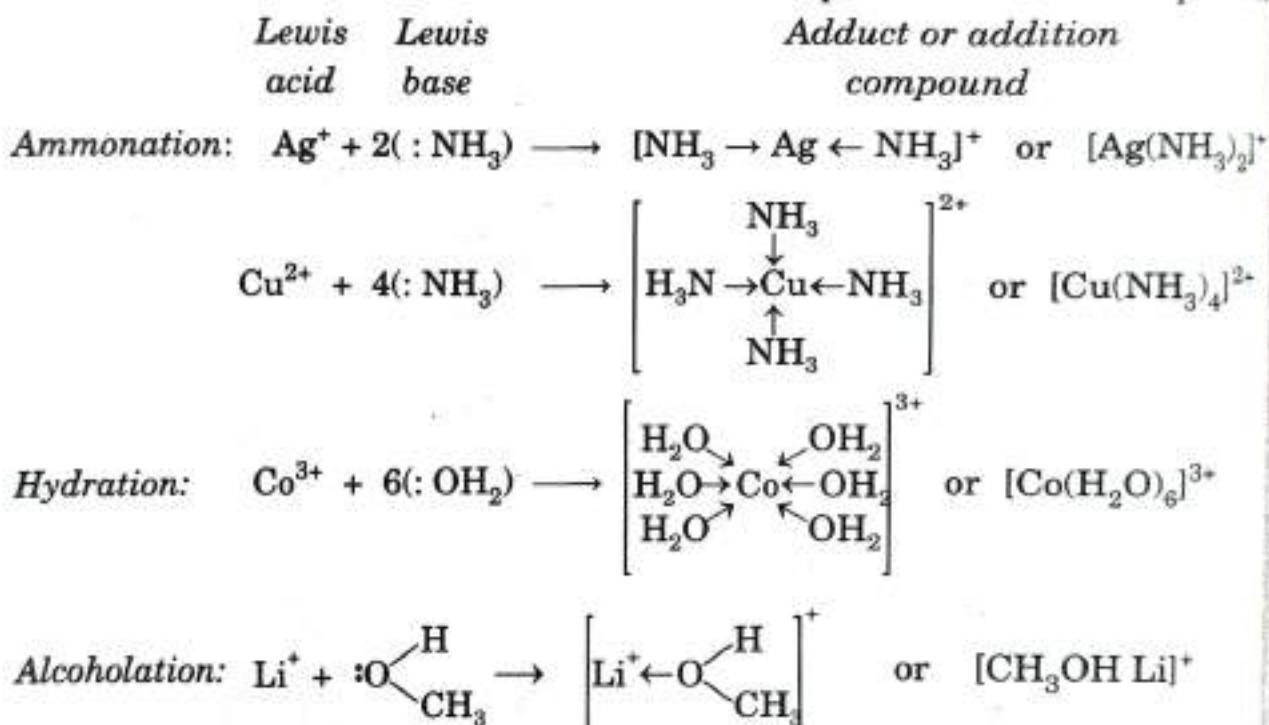
(v) H^+ ion has one vacant 1s orbital. Hence it can accept an electron pair donated by NH_3 molecule (Lewis base) to form NH_4^+ ion. Thus in the reaction between H^+ and NH_3 , H^+ ion acts as a Lewis acid.



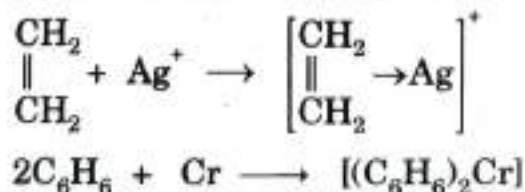
The formation of H_3O^+ ion can be shown as:



3. Simple cations. Theoretically all simple cations are potential Lewis acids. Reactions of some cations as Lewis acids with Lewis bases are shown below. It will be seen that these reactions are identical with those which produce Werner complexes.

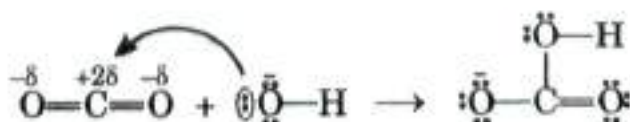


In coordination complexes of unsaturated organic compounds (e.g. C_2H_4 , C_2H_2 , C_6H_6 etc) e.g. $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ (Zeise's salt), $[\text{Cr}(\text{C}_6\text{H}_6)_2]$ etc. electron density from π -bond is donated to the metal ion. Thus the unsaturated organic compounds serve as Lewis bases and the metal ions act as Lewis acids. Examples are:



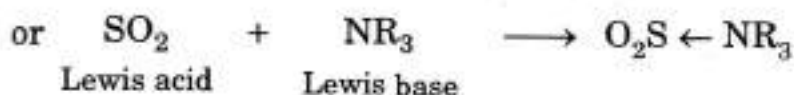
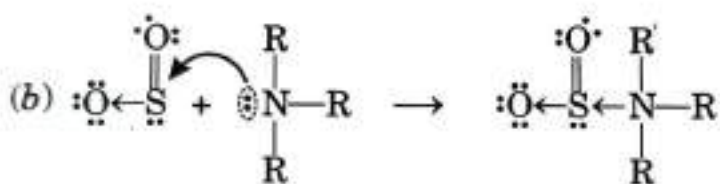
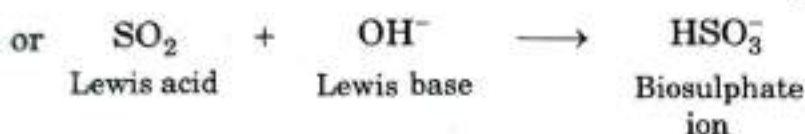
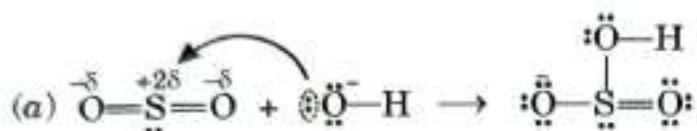
4. Molecules in which the central atom is bonded to two atoms of different electronegativities through one or more multiple bonds. Examples are given below:

(i) In CO_2 molecule ($\text{O}=\text{C}=\text{O}$), since O-atom is more electronegative than C-atom, this atom pulls the π electrons towards itself leaving a partial positive charge ($+\delta$) on C-atom. As a result C-atom becomes electron-deficient centre ($\text{O}=\overset{+\delta}{\text{C}}=\text{O}$) and hence acts as an electron acceptor (Lewis acid) towards Lewis base like OH^- ion which will donate its electron pair to C-atom to form bicarbonate ion, HCO_3^- .

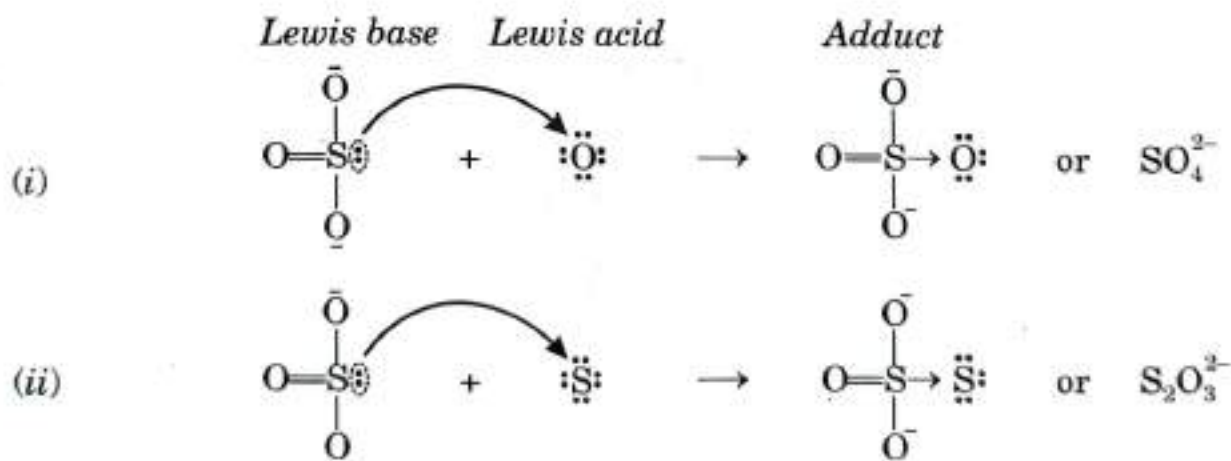




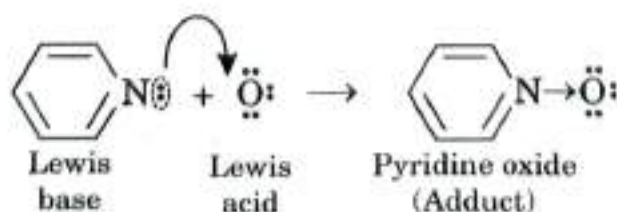
(ii) SO_2 also acts as a Lewis acid towards OH^- ion and NR_3 molecule



5. Elements with an electron sextet. Oxygen and sulphur atoms contain six electrons in their valence shell and can, therefore, be regarded as Lewis acids. The oxidation of SO_3^{2-} to SO_4^{2-} ion by oxygen and to $\text{S}_2\text{O}_3^{2-}$ ion by sulphur are the acid-base reactions.



The formation of pyridine oxide ($\text{C}_5\text{H}_5\text{N} \rightarrow \text{O}$) is an example of Lewis acid-base reaction in which pyridine ($\text{C}_5\text{H}_5\text{N}$) acts as a Lewis base and O-atom acts as a Lewis acid.



Classification of Lewis Bases.

Lewis bases can be classified as:

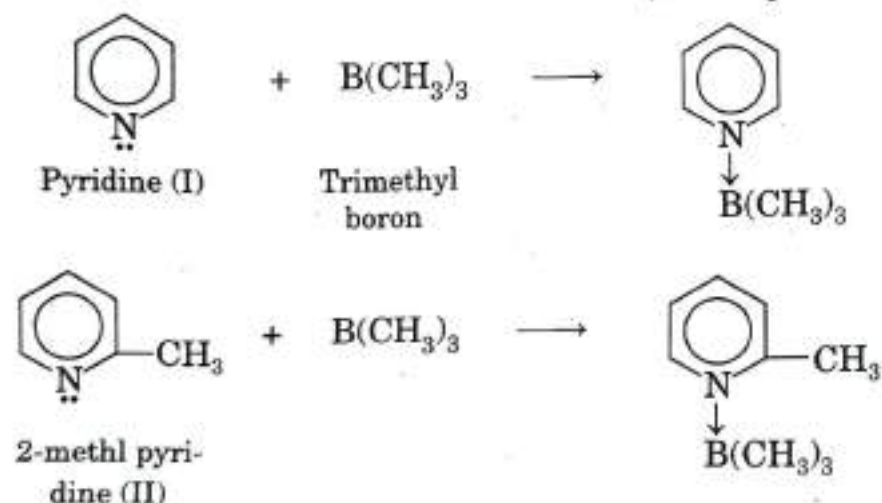
(i) Neutral molecules like NH_3 , $\text{R}-\text{NH}_2$, $\text{R}-\ddot{\text{O}}\text{H}$, $\text{H}-\ddot{\text{O}}-\text{H}$ etc., in which one of the atoms has got at least one lone pair of electrons.

(ii) All negative ions like F^- , Cl^- , Br^- , I^- , OH^- , CN^- , etc.

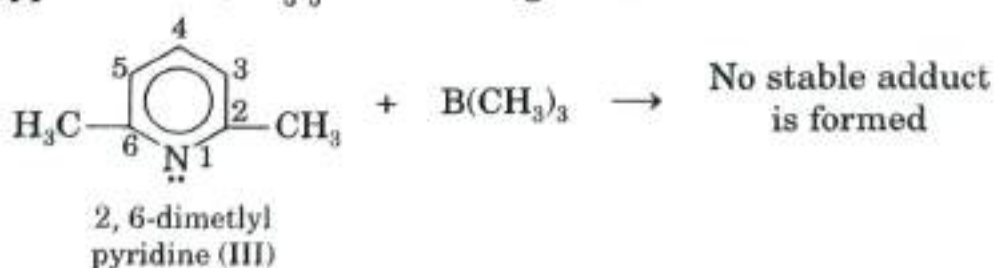
Steric Effect of Substituents in Lewis Acid-Base Reactions

It has been observed that due to the presence of a *lp* of electrons on N-atom, pyridine (I), 2-methyl pyridine (II) and 2, 6-dimethyl pyridine (III) show basic properties. Due to the inductive effect of $-\text{CH}_3$ groups, their basic property increases in the order: (I) < (II) < (III). It has been seen that (I) and (II) both react with the electron-deficient $\text{B}(\text{CH}_3)_3$ molecule to form stable acid-base adducts.

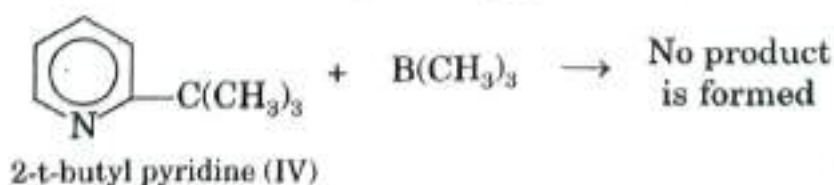
Lewis base *Lewis acid* *Lewis acid-base adduct*
(Stable product)



Although (III) is stronger Lewis base than (I) and (II) both, yet it does not form stable adduct with $\text{B}(\text{CH}_3)_3$. The non-formation of stable adduct is because of the fact that the overcrowding of two $-\text{CH}_3$ groups at 2- and 6-positions in (III) molecule hinders the approach of $\text{B}(\text{CH}_3)_3$ molecule to give stable adduct.

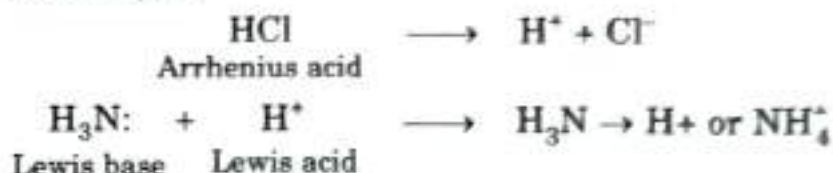


2-t-butyl pyridine (IV) also does not form stable acid-base adduct with $\text{B}(\text{CH}_3)_3$ because of the steric effect of t-butyl group, $-\text{C}(\text{CH}_3)_3$ at the 2-position of the pyridine.



Arrhenius Acids vs Lewis Acids

Arrhenius considered those substances as acids which could donate proton (H^+). Since proton can accept an electron pair from a base, *all Arrhenius acids are also Lewis acids*. For example:



Bronsted Bases vs Lewis Bases

According to Bronsted a base is a substance which accepts proton while according to Lewis, a base is any species which can donate an electron pair. Bronsted base can accept proton only when it has an unshared pair of electrons in it. *Thus all Bronsted bases are also Lewis bases*. This fact can be made evident from the following neutralisation reaction in which NH_3 behaves both as Bronsted base as well as Lewis base.



In this reaction, since NH_3 molecule accepts a proton (H^+), it behaves as a Bronsted base. At the same time, since NH_3 molecule also donates an electron pair to H^+ ion, this molecule (i.e. NH_3 molecule) behaves as a Lewis base.

Bronsted Acids vs Lewis Acids

There are many Lewis acids (e.g. SO_3 , halides of B, Al, Fe (III) and Zn) which cannot be treated as Bronsted acids. The central atom of these acids is electron-deficient and hence can accept a pair of electrons from a base to complete its octet.

Similarly HCl which is a Bronsted acid cannot be called a Lewis acid, since it has no vacant orbital to accept an electron pair from a base.

Solvent System vs Lewis System

Solvent system considers NH_4^+ ion as an acid and NH_2^- ion as a base in liq. NH_3 as shown below:



In the above reaction, NH_2^- ion donates a lone pair of electrons to NH_4^+ ion to produce two molecules of NH_3 . Since NH_4^+ ion is nothing but an ammoniated proton and the proton (H^+) can accept a lone pair of electrons from a base (i.e. NH_2^- ion), NH_4^+ and NH_2^- ions which are acid and base respectively in liquid NH_3 are also Lewis acid and Lewis base.

Factors Affecting the Relative Strength of Lewis Acids

Relative strength of Lewis acids depends mainly on the following factors:

1. Inductive effect of EWG and EDG The inductive effect caused by EWG increases the acid strength of Lewis acid while inductive effect caused by EDG

decreases the acid strength of Lewis acid. For example if H in BH_3 is replaced by F which is an EWG, acidic strength increases. Thus BF_3 is a stronger Lewis acid and than BH_3 ($\text{BF}_3 > \text{BH}_3$). On the other hand, if H in BH_3 is replaced by Me group which is an EDG, the acidic strength decreases. Thus Me_3B is weaker Lewis acid than BH_3 ($\text{Me}_3\text{B} < \text{BH}_3$) Thus the overall acidic strength of BH_3 , BF_3 and BMe_3 increases as:



Note. Experimentally it has been found that the acid strength of BF_3 , BCl_3 and BBr_3 molecules which are Lewis acids increases as:



This increasing order cannot be explained on the basis of electron-withdrawing inductive effect ($-I$ effect) of $-\text{F}$, $-\text{Cl}$ and $-\text{Br}$ groups present in the trihalide molecules as shown below.

Since $-I$ effect of halide groups decreases as $-\text{F} > -\text{Cl} > -\text{Br}$, the electron-accepting power (Lewis acid strength) of B-atom in BX_3 molecules ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) should also increase in the order:



This decreasing order which is based on $-I$ effect of halide groups is opposite to that shown at (i) which is experimentally observed order. Thus we see that the experimentally observed increasing order of acidic strength of BF_3 , BCl_3 and BBr_3 shown at (i) cannot be explained on the basis of inductive effect.

2. Electronegativity. Tetrahalides of Sn (SnCl_4 , SnBr_4 and SnI_4) are Lewis acids. The acid strength of these acids decreases as $\text{SnCl}_4 > \text{SnBr}_4 > \text{SnI}_4$. This decreasing order is due to the decrease in electronegativity of halogen atoms from Cl to I.

Note. It has been found experimentally that the Lewis acid strength of BX_3 molecules ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) which are Lewis acids decreases as:

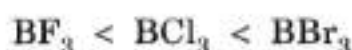


This order cannot be explained on the basis of electronegativity (EN) of halogen atoms. Due to the decrease in EN values of halogens from F to Br ($\text{F} > \text{Cl} > \text{Br}$), the Lewis acid strength of BX_3 molecules should decrease as:

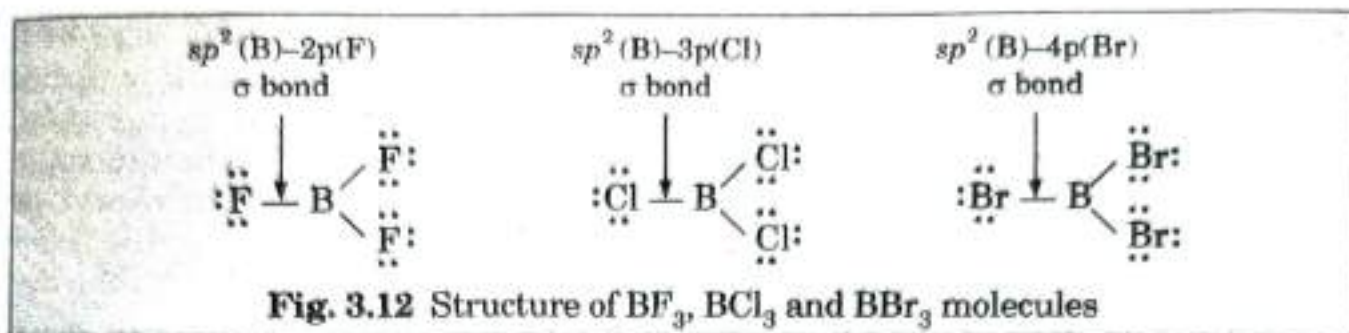


This order is opposite to the order shown at (i) which has been found experimentally. Thus we see that the experimentally observed increasing order of acidic strength of BF_3 , BCl_3 and BBr_3 shown of (i) cannot be explained on the basis of electronegativity values of halogen atoms.

3. Back donation in BF_3 , BCl_3 and BI_3 . It has been found experimentally that the Lewis acid strength of BF_3 , BCl_3 and BBr_3 molecules increases in the order:

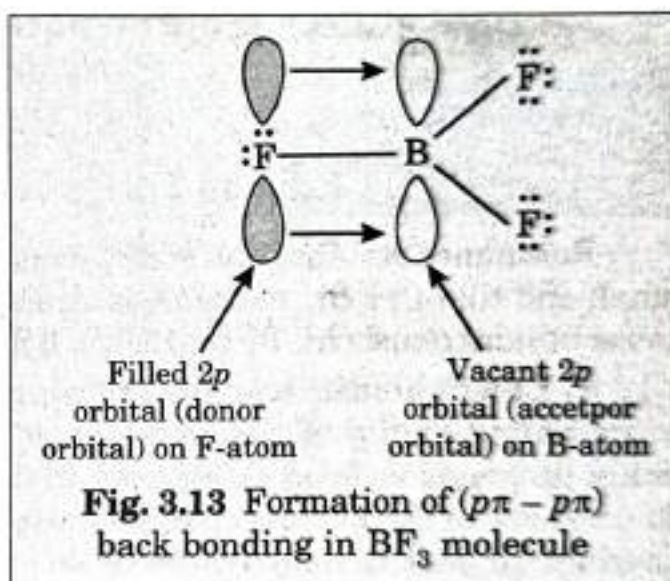


This order can neither be explained on the basis of inductive effect of halogen groups nor on the basis of EN values of halogen atoms. This order has been explained on the basis of the formation of dative bond or $p\pi - p\pi$ back bond (back donation) in BX_3 molecules. The structures of BF_3 , BCl_3 and BBr_3 molecules are given in Fig. 3.12.



In the structure of each of trihalide molecules, B -atom is sp^2 hybridised [$B^* = 2s^1 2p^1 2p^1 2p^0$] or $(sp)^1 (sp)^1 (sp)^1 2p^0$. Obviously B -atom has three singly-filled sp hybrid orbitals and one empty $2p$ orbital in its valence shell. In BF_3 molecule each of the three $B-F$ σ bonds is formed by the overlap between singly-filled sp^2 hybrid orbital on B -atom and singly-filled $2p$ orbital on F -atom. ($F = 2s^2 2p^2 2p^2 2p^1$). Thus each of the three $B-F$ bonds in BF_3 molecules is $sp^2(B) - 2p(F)$ σ -bond. In case of BCl_3 and BBr_3 molecules $B - \text{Cl}$ and $B - \text{Br}$ σ -bonds are $sp^2(B) - 3p(\text{Cl})$ and $sp^2(B) - 4p(\text{Br})$ σ -bonds. ($\text{Cl} = 3s^2 3p^2 3p^2 3p^1$, $\text{Br} = 4s^2 4p^2 4p^2 4p^1$).

Now let us take the example of BF_3 molecule to explain the formation of $p\pi - p\pi$ back bond in this molecule. We have already stated F -atom has one completely-filled $2s$ orbital and two completely-filled $2p$ orbitals ($F = 2s^2 2p^2 2p^2 2p^1$). One of the filled $2p$ orbitals on F -atom overlaps with the vacant $2p$ orbital (acceptor orbital) on B -atom and forms an additional $F \rightarrow B\pi$ bond which is a $2p^2(F) \rightarrow 2p^0(B)\pi$ bond. This bond is represented as $p\pi - p\pi$ bond and is called dative bond or $p\pi - p\pi$ back bond. Obviously $p\pi - p\pi$ bond is formed by the donation of an electron pair from the

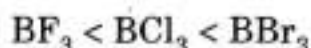


filled $2p$ orbital of F -atom to the vacant $2p$ orbital of B -atom (see Fig. 3.13). This is called **back donation**. Filled $2p$ orbital of F -atom is called **donor** $2p$ orbital and vacant $2p$ orbital on B -atom is called **acceptor** $2p$ orbital.

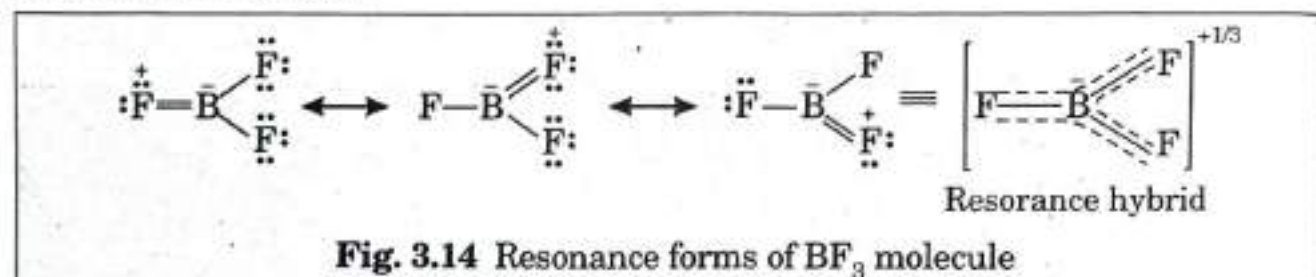
Due to the formation of $p\pi - p\pi$ back bond, electronic charge from the filled $2p$ orbital of F -atom is shifted to the vacant $2p$ orbital of B -atom. The shifting of electronic charge from F -atom to B -atom decreases the electron-accepting power (electron-accepting tendency) or Lewis acid strength of B -atom in BF_3 molecule.

The back bonding in BF_3 molecule is supported by the fact that the observed $B - F$ bond length ($=130\text{pm}$) in BF_3 molecule is much less than the sum of the covalent radii of B and F atoms ($B = 85 \text{ pm}$ and $F = 64 \text{ pm}$, sum $= 85 + 64 = 149 \text{ pm}$). Here it should be noted that since $2p$ orbital (filled) of F atom and $2p$ orbital (empty) of B atom have almost the same size, the overlap between these two $2p$ orbitals to form $2p^2(F) \rightarrow 2p^0(B)\pi$ bond is very effective. In case of BCl_3 and BBr_3 molecules $p\pi - p\pi$ back bonds are $3p^2(\text{Cl}) \rightarrow 2p^0(\text{B})$ and $4p^2(\text{Br}) \rightarrow 2p^0(\text{B}) \pi$ bonds respectively.

Now since $3p$ orbital of Cl and $4p$ orbital of Br both have larger size than $2p$ orbital of B-atom, $3p^2(\text{Cl}) - 2p^0(\text{B})$ overlap in BCl_3 molecule and $4p^2(\text{Br}) - 2p^0(\text{B})$ overlap in BBr_3 molecule are not so effective as $2p^2(\text{F}) - 2p^0(\text{B})$ overlap in BF_3 molecule. Thus in case of BCl_3 and BBr_3 molecules the shifting of electronic charge from the filled $3p$ orbital of Cl-atom and from the filled $4p$ orbital of Br-atom to the vacant $2p$ orbital of B-atom is much less than the shifting of electronic charge from the filled $2p$ orbital of F atom to the vacant $2p$ orbital of B atom. Hence we can say that the electron-accepting power of B-atom in BCl_3 and BBr_3 is more than that of B-atom in BF_3 . In other words, the electron-accepting power or Lewis acid strength of the three boron trihalides increases in the order:



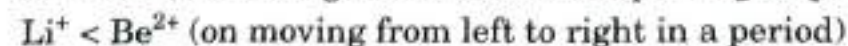
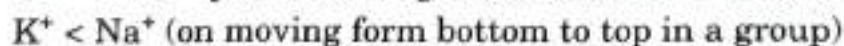
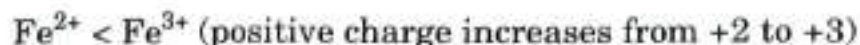
The increasing order of Lewis acid strength of BX_3 molecules from BF_3 to BBr_3 can also be explained on the basis of resonance stabilisation of BX_3 molecules. Back bonding in BF_3 molecule can oscillate among the three B-F bonds in BF_3 molecule as shown in Fig. 3.14.



Resonance stabilisation of BF_3 molecule is large while that in BCl_3 molecule is small and that in BBr_3 molecule is still smaller. Hence Lewis acid strength of BX_3 molecules increases as: $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$.

4. Lewis acidic strength of simple cations. The Lewis acid strength or coordinating ability of the simple cations which, according to Lewis, are Lewis acids, increases with (a) an increase in the positive charge carried by the cation (b) an increase in the nuclear charge for atoms in any period of the periodic table (c) a decrease in ionic radius (d) a decrease in the number of shielding electron shells.

Evidently the acid strength of simple cations increases for the elements on moving from left to right in a period and from bottom to top in a group of periodic table. Thus:

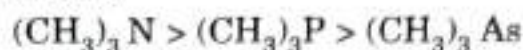


Lewis Acid Strength of Metal Cations in Gas Phase

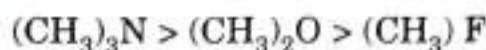
Acidity of metal cations in gas phase can be measured from the values of EA of metal cation. Lower is the value of EA of a given metal cation, lower is the acidity of the cation. For example since the value of EA of K^+ ion (= 420 KJ/mol) is lower than that of Ca^{2+} ion (= 1150 KJ/mol), the former (*i.e.* K^+ cation) is a weaker acid than the latter (*i.e.* Ca^{2+} cation)

Relative Strength of Lewis Bases

As we move down a group, the basic strength of Lewis bases decreases. For example the basic strength of $(\text{CH}_3)_3\text{N}$, $(\text{CH}_3)_3\text{P}$ and $(\text{CH}_3)_3\text{As}$ which are Lewis bases decreases in the order:



On moving from left to right in a period, the basic strength of Lewis bases decreases. For example:



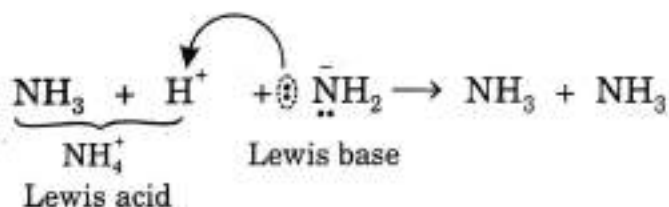
The decrease in basic strength is due to the increase in electronegativity of the central atoms from N to F.

Behaviour of NH_4^+ and NH_2^- Ions According to Solvent System and Lewis System

Solvent system considers NH_4^+ ion as an acid and NH_2^- ion as a base in liquid NH_3 as shown below:



Now since NH_4^+ ion is an ammoniated proton, the above equation can also be written as:



In this reaction, since NH_2^- ion donates an electron pair to H^+ ion, NH_2^- ion acts as a Lewis base and H^+ ion or NH_4^+ ion which accepts an electron pair behaves as a Lewis acid. Thus we see that NH_4^+ and NH_2^- ions which behave as acid and base respectively in liq. NH_3 also behave as Lewis acid and Lewis base.

Utility of Lewis Concept

- (i) This concept also includes those reactions in which no protons are involved.
- (ii) Lewis concept is more general than the Bronsted-Lowry concept (*i.e.* protonic concept) in that acid-base behaviour is not dependent on the presence of one particular element or on the presence or absence of a solvent.
- (iii) It explains the long accepted basic properties of metallic oxides and acidic properties of non-metallic oxides.
- (iv) This theory also includes many reactions such as gas-phase, high temperature and non-solvent reaction as neutralisation processes.
- (v) The Lewis approach is, however, of great value in cases where the protonic concept is inapplicable, for example, in reaction between acidic and basic oxide in fused state.

Drawback of Lewis Concept

Lewis concept suffers from the following drawbacks.

(i) Lewis concept is so general that it considers every reaction forming a coordinate bond to be acid-base reaction. This however, may not be always true, since according to this concept, even some metals are acids, e.g., nickel is acid because it forms the coordination compound with CO, *i.e.*, $\text{Ni}(\text{C}\equiv\text{O})_4$, called nickel tetracarbonyl.

(ii) The necessary requirement in Lewis concept is the formation of a coordinate bond between the acid and base. However, the well known acids like HCl and H_2SO_4 do not form any coordinate bond and, therefore, should not be acids according to this concept.

(iii) Acid-base reactions are usually fast but formation of coordination compound is slow. Hence, it does not fit in the acid-base concept.

(iv) The catalytic activity of an acid is due to H^+ (*aq*) ion. Since the presence of hydrogen is not an essential requirement for a Lewis acid, many Lewis acids will not have this property.

(v) The drawback of Lewis concept compared to Arrhenius concept or Bronsted concept is that there is no simple method of measuring the relative strength of bases as electron donors or of acids as electron acceptors.

Summary: Definition of Acids and Bases According to Different Concepts

(i) **Arrhenius concept (Water ion system)** An acid is a species that gives H^+ or H_3O^+ ions in aqueous solution. A base is a species that gives OH^- ions in aqueous solution.

(ii) **Bronsted-Lowry concept (Proton donor-acceptor system).** An acid is a species which can donate a proton (H^+ ion) to other substance, *i.e.* an acid is a proton donor. A base is species which can accept a proton donated by an acid, *i.e.* base is a proton acceptor.

(iii) **Lux-Flood concept:** The species that loses (donates) an O^{2-} ion behaves as a base and the species that accepts an O^{2-} ion is an acid, *i.e.* a base is O^{2-} ion donor and an acid is O^{2-} ion acceptor.

(iv) **Solvent-system concept.** An acid is a substance which, by dissolution in the solvent, gives the solvent cation (acid ion) obtained by the auto-ionisation of the solvent itself. A base is a substance which, by dissolution in the solvent, gives the solvent anion (base ion) obtained by the ionisation of the solvent itself.

(v) **Lewis concept (Electron donor-acceptor system).** An acid is a species that can accept an electron pair, *i.e.* an acid is an electron pair acceptor. A base is a species that can donate an electron pair, *i.e.* base is an electron pair donor.

UNIVERSITY QUESTIONS

1. Write a short note on "Arrhenius concept of acids and bases." (Ranchi 2010)
2. Write conjugate acids and bases of H_2O and HCO_3^- (Kota 2006)
3. (a) Arrange the following conjugate bases in the increasing order of their basic strength : ClO_4^- , ClO^- , ClO_3^- and ClO_2^- .

4

CHAPTER

Hard and Soft Acids and Bases (HSAB)

Hard and Soft Acids and Bases

According to Lewis concept of acids and bases, a Lewis and Lewis base reaction is the combination of a Lewis acid and a Lewis base to form complex ion (adduct). In this reaction the filled orbital on Lewis base and a vacant orbital on Lewis acid combine together to form a stable complex.

Coordination chemists studied the relative reactivities of a large number of ligands (Lewis bases) with different metal ions (Lewis acids) and found that certain ligands form complexes with heavier metal ions like Ag^+ , Hg^{2+} , Pd^{2+} , Pt^{2+} , etc. while other ligands form complexes with metal ions like Be^{2+} , Al^{3+} , Ti^{4+} , etc.

Based on the preferential tendency of ligands (Lewis bases) and metal ions (Lewis acids) to form stable complexes, the metal ions as well as ligands have been classified by Pearson (1963) into two categories each. Metal ions (Lewis acids) are categorised as **hard acids** and **soft acids**, and the ligands (Lewis bases) are categorised as **hard bases** and **soft bases**.

There are Lewis acids and Lewis bases which are neither too hard nor too soft. such acids and bases are called **border line acids** and **border line bases** respectively.

Table 4.1. Some common hard, soft and border line Lewis acids

<i>Hard Acids</i> (a type metal ions)	<i>Soft Acids</i> (b type metal ions)	<i>Border Line Acids</i>
H^+ , Li^+ , Na^+ , K^+ , Mn^{2+} , Co^{2+}	Cu^+ , Ag^+ , Au^+ , Tl^+ , Hg^+ , CH_3Hg^+	Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+}
Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ni^{2+}	Pt^{2+} , Cd^{2+} , Pd^{2+} , Hg^{2+} , Ir^{2+} , Pt^{4+} , CH_3^+	Zn^{2+} , Sb^{3+} , Bi^{3+} , NO^+
Al^{3+} , Sc^{3+} , Ga^{3+} , In^{3+} , La^{3+}	Ti^{3+} , BH_3 , GaCl_3 , GaBr_3	SO_2 , $\text{B}(\text{CH}_3)_3$, GaH_3
Cr^{3+} , Co^{3+} , Fe^{3+} , As^{3+} , Ce^{3+}	GaI_3 , InCl_3 , Cs^+ , Rh^{2+}	
Si^{4+} , Ti^{4+} , Zr^{4+} , Th^{4+} , Pu^{4+}	I^+ , Br^+ , HO^+ , RO^+ , CH_3Cd^+ , $\text{C}_2\text{H}_5\text{Hg}^+$	
UO_2^{2+} , VO_2^{2+} , MoO_3^{3+} , Cu^{2+}		
BF_3 , BCl_3 , AlCl_3 , AlH_3 , $\text{Al}(\text{CH}_3)_3$, Zn^{2+}	I_2 , Br_2 , ICN	
Cl^{3+} , Cl^{7+} , I^{5+} , I^{7+}	O , Cl , Br , I , N	
RCO^+ , CO_2 , NC^+ , HX	M° (Metal atom)	
HX (Hydrogen bonding molecules)	CH_2 , Carbenes	

Some common metal ions which act as hard, soft or border line acids are given in Table 4.1. According to Ahrlund and Chatt hard acids are **a** type metal ions or acceptors while soft acids are **b** type metal ions or acceptors.

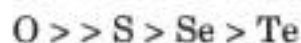
List of some common hard, soft and border line bases is given in Table 4.2.

Table 4.2. Some common hard, soft and border line bases

<i>Hard bases</i>	<i>Soft bases</i>	<i>Border line bases</i>
$\text{NH}_3, \text{RNH}_2, \text{N}_2\text{H}_4, \text{H}^+, \text{CF}_3^+$	$\text{H}^-, \text{R}^-, \text{C}_2\text{H}_4, \text{C}_6\text{H}_6, \text{CH}_3^+$	$\text{C}_6\text{H}_5\text{NH}_2, \text{C}_5\text{H}_5\text{N}$
$\text{N}_2\text{O}, \text{OH}^-, \text{O}^{2-}, \text{ROH}, \text{RO}^-, \text{R}_2\text{O}$	$\text{CN}^-, \text{RNC}, \text{CO}, \text{R}_2\text{S}$	$\text{N}_2, \text{N}_3^-, \text{NO}_2^-$
$\text{CH}_3\text{COO}^-, \text{CO}_3^{2-}, \text{NO}_3^-$	$\text{S}_2\text{O}_3^{2-}, \text{SCN}^-, \text{R}_3\text{P}$	Br^-
$\text{PO}_4^{3-}, \text{SO}_4^{2-}, \text{ClO}_4^-, \text{F}^-, \text{Cl}^-$	$\text{R}_3\text{As}, \text{I}^-, \text{SH}^-, \text{S}^{2-}, \text{SO}_3^{2-}$	

Characteristics of Hard Acids

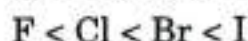
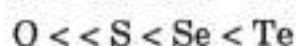
- (i) Ahrlund and Chatt have termed hard acid metal ions as class **a** metals or acceptors.
- (ii) In general, alkali metal ions, alkaline earth metal ions, lighter and more highly charged metal ions are hard acids.
- (iii) Hard acids have generally high positive oxidation states or high positive charge.
- (iv) Hard acids have smaller acceptor atoms.
- (v) Hard acids do not contain large number of valence electrons and hence their valence electrons cannot be easily distorted, *i.e.* hard acids cannot be easily polarised.
- (vi) Hard acids have high EN.
- (vii) Hard acids bind strongly to proton.
- (viii) Hard acids usually form stable complexes with bases that bind well with protons.
- (ix) The tendency of different donor atom (ligands) to form complexes with hard acids follows the order:



Characteristics of Soft Acids

- (i) Ahrlund and Chatt have termed soft acid metal ions as class **b** metals or acceptors.
- (ii) In general soft acids are heavier transition metal ions.
- (iii) Soft acids have large acceptor atoms.
- (iv) Soft acids have usually low (or even zero) positive oxidation state.
- (v) Soft acids have large number of valence electrons and therefore, their valence electrons can easily be distorted, *i.e.* soft acids can be easily polarised.

- (vi) Soft acids have low EN.
- (vii) Soft acids form stable complexes with bases that are highly polarisable, are good reducing agents and not necessarily good bases towards the proton.
- (viii) The tendency of different donor atoms (ligands) to form complexes with soft acids follows the order:



Important Points

- (i) If donor atoms of most common bases (ligands) are arranged in the increasing order of their electronegativity, the following order is obtained.

As	P	<	C	Se	S	I	<	Br	<	N	Cl	<	O	<	F
2.0	2.1	<	2.5	2.4	2.5	2.5	<	2.8	<	3.0	3.0	<	3.5	<	4.0

Soft acids will form more stable complexes with left hand donor atoms of this series and hard acids will form more stable complexes with right hand donor atoms of this series.

- (ii) It should be noted that all hard acids are not equally hard. Similarly, all soft acids are not equally soft. For example Cu^+ ion is a harder acid than Mn^{2+} ion because of smaller size of Cu^+ ion. Similarly, Li^+ ion is a harder acid than Cs^+ ion because of smaller size of Li^+ ion.
- (iii) Metals and non-metals in lower oxidation states behave as soft acids while the same species in higher oxidation states behave as hard acids.

Characteristics of Hard Bases

- (i) Hard bases are usually anions or neutral molecules.
- (ii) Donor atoms present in hard bases have high electronegativity (EN).
- (iii) Donor atoms of hard bases have low polarisability, *i.e.* donor atoms of hard bases cannot be easily polarised.
- (iv) Donor atoms are hard to oxidise, *i.e.* donor atoms cannot be easily oxidised.
- (v) Hard bases hold on to their valence electrons strongly. Thus, hardness of hard bases is associated with a highly held electron shell with little tendency to polarise.
- (vi) Hard bases have completely filled low energy orbitals.
- (vii) Hard bases strongly link to the proton.
- (viii) Hard bases prefer to coordinate with hard acids.

Characteristics of Soft Bases

- (i) Soft bases are usually anions or neutral molecules.
- (ii) Donor atoms in soft bases have low EN.
- (iii) Donor atoms have high polarisability, *i.e.* donor atoms of soft bases can be easily polarised.

- (iv) Soft bases can easily be oxidised.
- (v) Soft bases hold on to their valence electrons rather loosely. Thus softness of soft bases is associated with a loosely bound polarisable electron shell.
- (vi) Soft bases contain empty low energy orbitals.
- (vii) Soft bases prefer to combine with soft acids.

It should be noted that all the bases containing the same donor atom are not equally hard. For example the hardness of $C_6H_5NH_2$, $(C_6H_5)_2NH$ and NH_3 bases is in the order: $NH_3 > C_6H_5NH_2 > (C_6H_5)_2N$. In fact, $(C_6H_5)_2N$ is a soft base.

Characteristics of Border Line Acids and Border Line Bases

The properties (*e.g.* size, oxidation states, polarisability, etc.) of border line acids and border line bases are neither too low nor too high. These properties are intermediate between the properties of hard/soft acids and hard /soft bases.

Pearson's HSAB Principle

In 1963 Pearson proposed a rule for predicting the feasibility of a given reaction. This rule states:

A given reaction **is feasible** in which a hard acid reacts with a hard base and a soft acid reacts with a soft base, *i.e.* according to HSAB principle, only that reaction is feasible (*i.e.* only that reaction proceeds from left to right) in which the products are formed by *hard acids-hard base* and *soft acid-soft base combinations*. In other words, we can say that the reaction in which the products are formed by *hard acid-soft base* or *soft acid-hard base combinations* is not feasible.

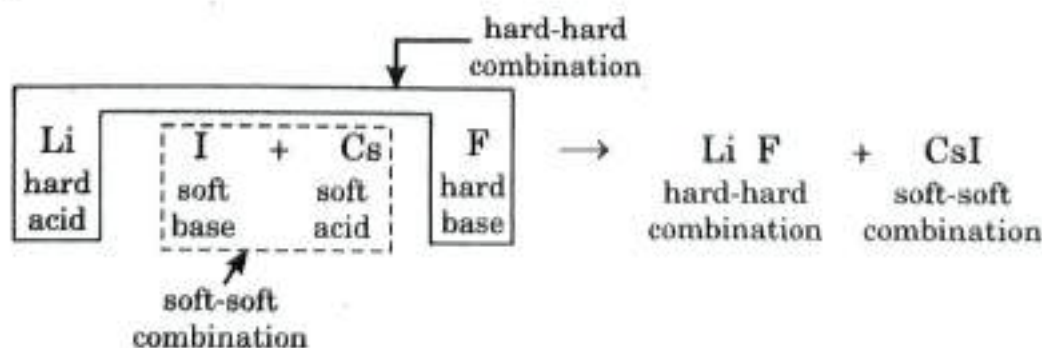
OR

A given reaction **is feasible** in which the products formed in the reaction are either hard acid-hard base or soft acid-soft base combinations.

OR

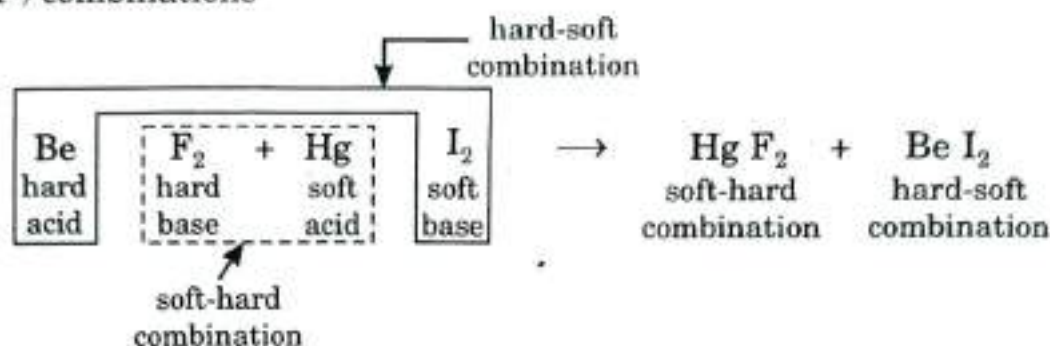
A given reaction **is not feasible** in which the products formed in the reaction are either hard acid-soft base or soft acid-hard base combinations.

Illustrative Examples : (i) The following reaction is feasible, since a hard acid (Li^+) combines with a hard base (F^-) and a soft acid (Cs^+) combines with a soft base (I^-) to form LiF (hard – hard combination) and CsI (soft – soft combination) respectively.

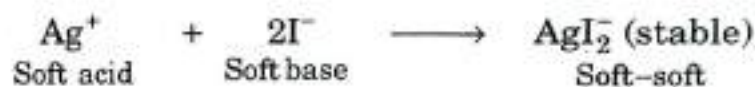


The reaction given above is feasible since the products (LiF and CsI) formed are hard acid (Li^+) – hard base (F^-) and soft acid (Cs^+) – soft base (I^-) combinations

- (ii) The following reaction is not feasible, since the products (HgF_2 and BeI_2) formed are soft acid (Hg^{2+}) - hard base (F^-) and hard acid (Be^{2+}) - soft base (I^-) combinations



- (iii) The following reaction is feasible, since soft acid (Ag^+) combines with a soft base (I^-) to form AgI_2^- (product) which is a soft acid (Ag^+) - soft base (I^-) combination.



- (iv) The following reaction is not feasible, since soft acid (Ag^+) combines with a hard base (F^-). According to HSAB principle, this type of combination does not give any product.



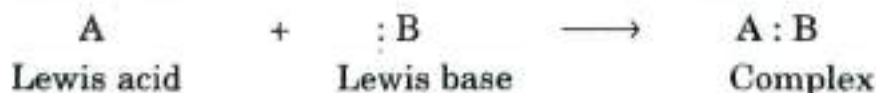
Also, since the product (AgF_2^-) is a soft acid (Ag^+) - hard base (F^-) combination, the reaction is not feasible.

Applications of HSAB Principle

HSAB principle has several applications some of which are discussed below:

1. Relative Stability of Complexes

Pearson (1963) has explained the relative stability of complexes on the basis of HSAB principle. Consider the formation of $\text{A} : \text{B}$ complex by the combination of A (Lewis acid) and $:\text{B}$ (Lewis base) as shown below:

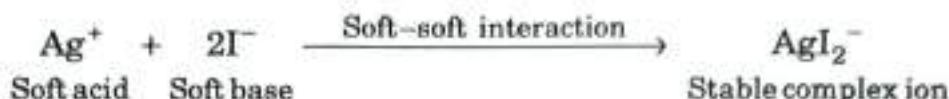


According to HSAB principle the complex, $\text{A} : \text{B}$ would be the most stable, if A (Lewis acid) and B (Lewis base) are either both hard or are both soft, i.e., hard acid + hard base and soft acid + soft base combinations give most stable complex.

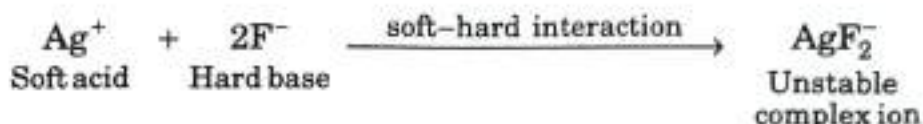
The complex, $\text{A} : \text{B}$ would be least stable, if A (Lewis acid) is hard and B (Lewis base) is soft or *vice versa*, i.e. hard acid + soft base and soft acid + hard base combinations give least stable complex.

Examples (i) AgI_2^- is a stable complex ion but AgF_2^- is an unstable complex ion. This can be explained as follows:

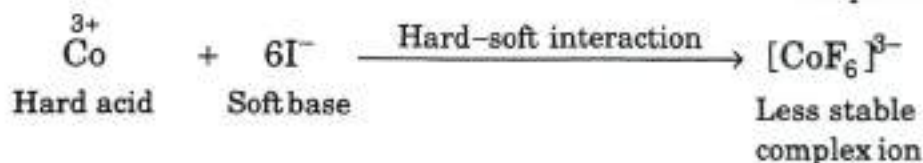
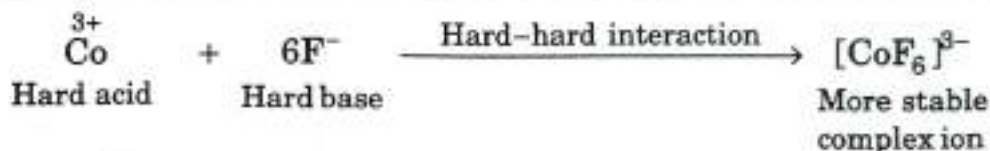
Since Ag^+ ion is soft acid and I^- ion is a soft base, the combination of these ions gives stable complex ion, AgI_2^-



Since Ag^+ ion is a soft acid and F^- ion is a hard base, the combination of these ions gives unstable complex ion, AgF_2^-



(ii) $[\text{CoF}_6]^{3-}$ is more stable than $[\text{CoI}_6]^{3-}$. This can be explained as follows:



(iii) Complex ions of a given metal ion having a combination of soft ligands (soft bases) and hard ligands (hard bases) are unstable while the complex ions of the same metal ion having a combination of soft ligands or hard ligands are stable.

Example: $[\text{Co}(\text{CN})_5\text{F}]^{3-}$ and $[\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$ are unstable complex ions while $[\text{Co}(\text{CN})_5\text{I}]^{3-}$ and $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$ are stable complex ions. This observation is due to the fact that CN^- and I^- both are soft ligands (soft bases) and NH_3 and F^- both are hard ligands (hard bases).

2. Formation of Complexes with Ambidentate Ligands

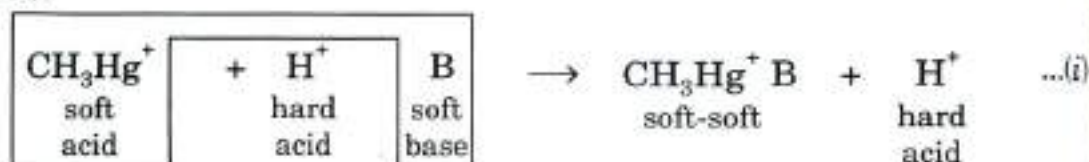
HSAB Principle can explain the formation of complexes with ambidentate ligands. An ambidentate ligand is a unidentate (monodentate) ligand which can coordinate to the metal ion through either of its two coordinating atoms: For example, SCN^- ion is an ambidentate ligand, since it can coordinate to the metal ion either through S-atom or through N-atom. When this ligand gets coordinated to the metal ion through S-atom, thiocyanato complexes are formed. When this ligand is coordinated to the metal ion through N-atom, isothiocyanato complexes are formed. In this ligand N-atom is a hard base and S-atom is a soft base. This ligand forms thiocyanato complexes of $[\text{M}(\text{SCN})_4]^{2-}$ type with Rh^{2+} , Ir^{2+} , Pd^{2+} , Pt^{2+} , etc. cations (soft acids) by coordinating through S-atom (soft base) to form M – SCN bond. This ligand forms isothiocyanato complexes of $[\text{M}(\text{NCS})_4]^{2-}$ type with Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} cations (hard acids) by coordinating through N-atom (hard base) to form M – NCS bond.

Example: We have said above that Co^{2+} ion forms isothiocyanato complex, $[\text{Co}(\text{NSC})_4]^{2-}$ while Pd^{2+} ion forms thiocyanate complex, $[\text{Pd}(\text{SCN})_4]^{2-}$. The formation of these complexes can be explained on the basis of HSAB principle. According to this principle, since Co^{2+} ion is a *hard acid*, it prefers to coordinate to *hard base N-atom* of the ligand to form $[\text{Co}(\text{NSC})_4]^{2-}$ ion which contains $\text{Co}-\text{NCS}$ bond (*hard acid-hard base interaction*). Since Pd^{2+} ion is a *soft acid*, it prefers to coordinate to *soft base S-atom* of the ligand to form $[\text{Pd}(\text{SCN})_4]^{2-}$ which contain $\text{Pd}-\text{SCN}$ bond (*Soft acid-soft base interaction*).

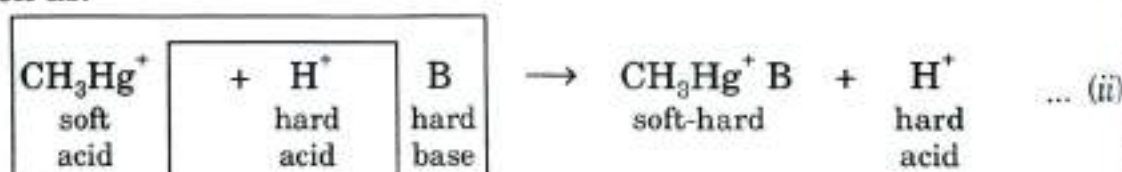
3. Predication of Hardness and Softness of an Acid and a Base.

HSAB principle is useful in predicting whether a given base or an acid is hard or soft. Suppose we want to predict whether a given base B present in HB is a hard base or a soft base. For this let us consider the reaction between CH_3Hg^+ and HB. CH_3Hg^+ is a soft acid. In HB, H^+ ion is a hard acid and B may be a soft base or a hard base.

If B is a soft base, then the reaction between CH_3Hg^+ and HB can be written as:



If B is a hard base, then the reaction between CH_3Hg^+ and HB can be written as:

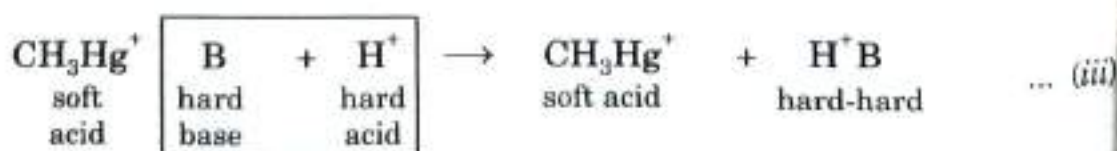


It may be noted that the products formed in both the reactions are the same. Now let us decide which of the above two reactions is feasible. This can be decided as follows:

In reaction (i), since $\text{CH}_3\text{Hg}^+ \text{B}$ (product) is formed by soft acid (CH_3Hg^+) – soft base (B) interaction, this reaction is **feasible** in accordance with HSAB principle. In other words we say that if reaction (i) is feasible (*i.e.* proceeds from left to right), the base, B is a **soft base**.

In reaction (ii), since $\text{CH}_3\text{Hg}^+ \text{B}$ (product) is formed by soft acid (CH_3Hg^+) – hard base (B) interaction, this reaction is **not feasible** as suggested by HSAB principle. In other words we say that if the reaction (ii) is not feasible (*i.e.* does not proceed from left to right), the base, B is a **hard base**.

Now let us consider reaction (ii) proceeding from right to left as written below:

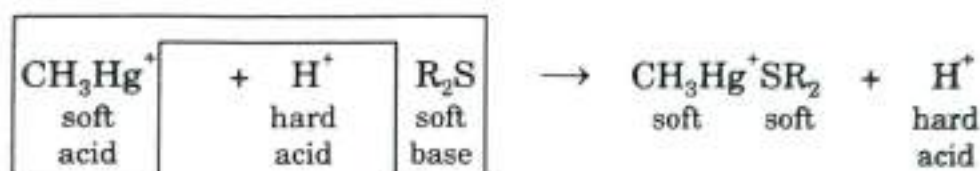


In reaction (iii), since $\text{H}^+ \text{B}$ (product) is formed by hard acid (H^+) – hard base (B) interaction, this reaction is **feasible** (HSAB principle). In other words we say that if reaction (ii) proceeds from right to left, B is a **hard base**.

Solved Examples. (i) Predict whether R_2S is a soft base or a hard base in the following reaction which proceeds from left to right.



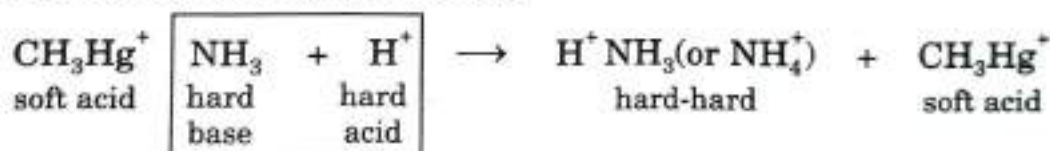
Ans: We know that CH_3Hg^+ is a soft acid and H^+ is a hard acid. Since the reaction proceeds from left to right, the formation of $CH_3Hg^+SR_2$ (product) should take place through soft acid (CH_3Hg^+) – soft base (R_2S) interaction (HSAB principle). For this interaction R_2S must be a **soft base**. Thus the given reaction can be written as:



(ii) Predict whether NH_3 is a soft base or a hard base in the following reaction which proceeds from left to right.



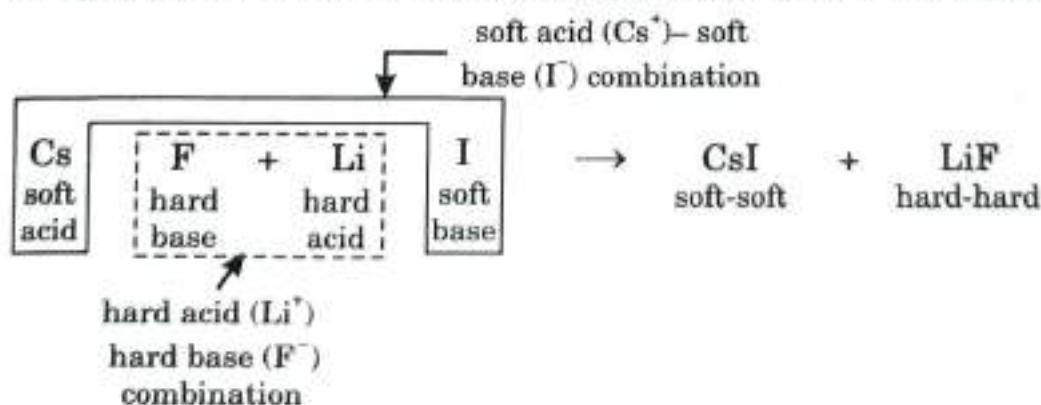
Ans. We know that CH_3Hg^+ and H^+ are soft acid and hard acid respectively. Since this reaction proceeds from left to right, the formation of NH_4^+ (product) should take place through hard acid (H^+) – hard base (NH_3) interaction (HSAB principle). For this interaction NH_3 must be a **hard base**. Thus the given reaction can also be written as:



4. Predicting Feasibility of a Reaction.

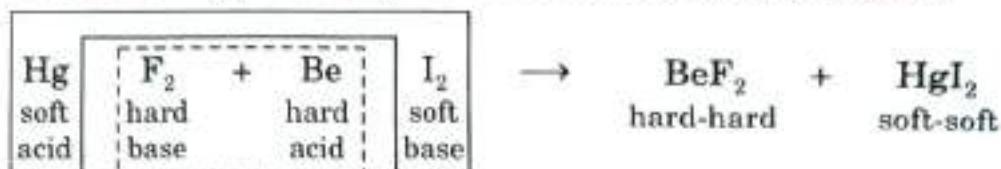
According to HSAB principle only those reactions are feasible (*i.e.* only those reactions proceed from left to right) in which products are formed by hard – hard and soft – soft combinations. The reactions in which products are formed by hard – soft and soft – hard combinations are not feasible.

Examples: (i) The following reaction proceeds from left to right.



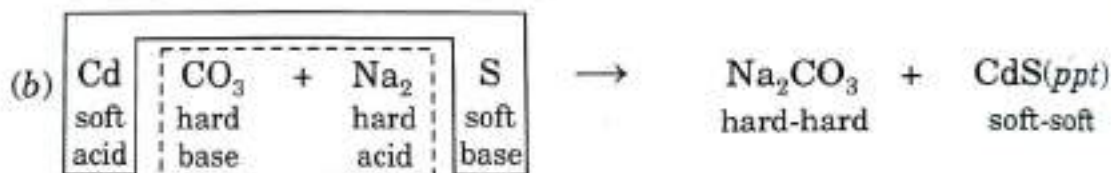
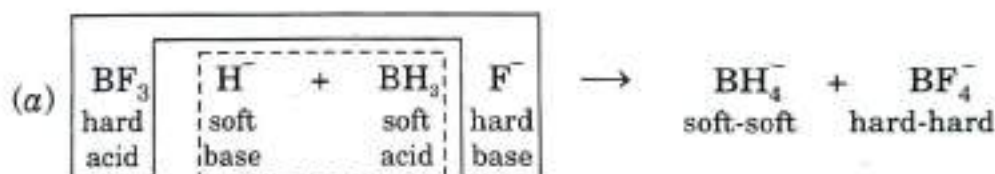
Explanation. In CsF , Cs^+ (soft acid) is combined with F^- (hard base) while in LiI , Li^+ (hard acid) is combined with I^- (soft base). CsI (soft + soft) and LiF (hard + hard) (products) are obtained by soft – soft and hard – hard combinations.

(ii) The following reaction proceeds in the forward direction

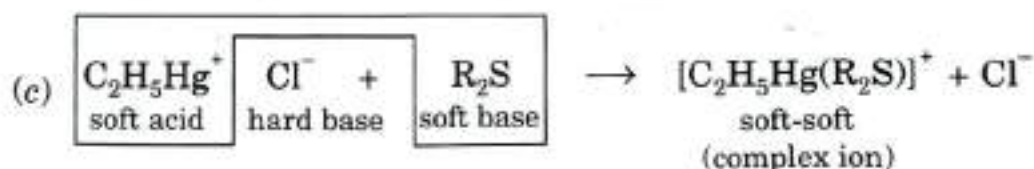


Explanation: In HgF_2 , Hg^{2+} (soft acid) is combined with F^- (hard base) while in BeI_2 , Be^{2+} (hard acid) is combined with I^- (soft base). BeF_2 (hard-hard) and HgI_2 (soft-soft) (products) are obtained by hard-hard and soft-soft combinations.

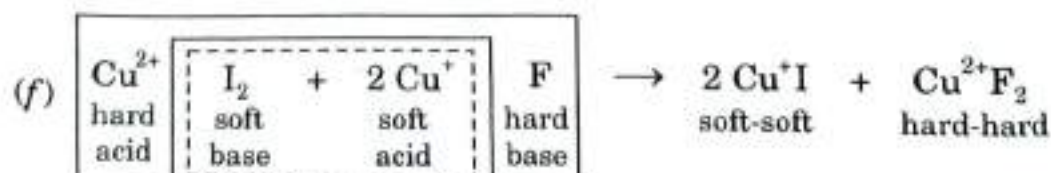
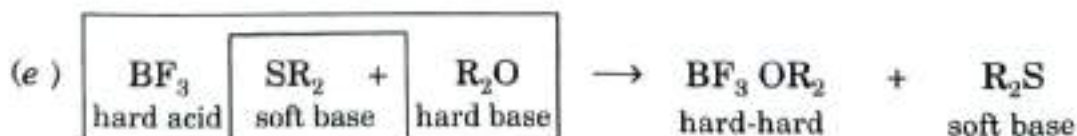
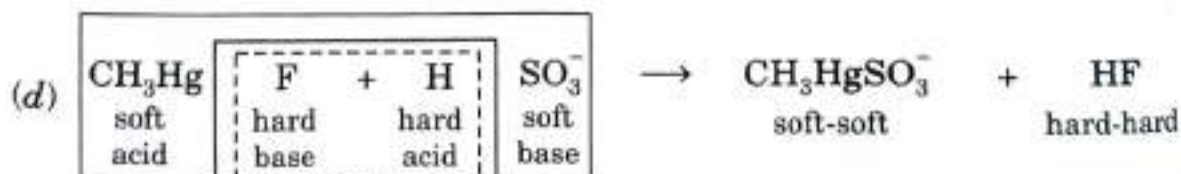
(iii) Other examples of reactions which proceed from left to right are given below:



In this reaction the ppt. of CdS is obtained by the combination of Cd^{2+} ion (soft acid) and S^{2-} ion (soft base).



In this reaction, $\text{C}_2\text{H}_5\text{Hg}^+$ (soft acid) combines with R_2S (soft base) to form the complex ion, $[\text{C}_2\text{H}_5\text{Hg}(\text{R}_2\text{S})]^+$.



5. Direction of Reaction

Consider the following reactions



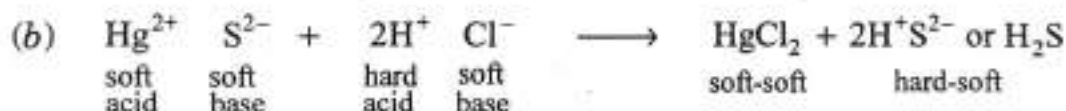
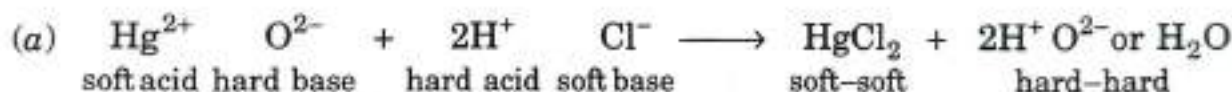
In reaction (a), since $\text{H}^+ \text{OH}^-$ or H_2O (product) is obtained by hard acid (H^+) – hard base (OH^-) interaction, this reaction proceeds from left to right.

In reaction (b), since $\text{H}^+ \text{SH}^-$ or H_2S (product) is obtained by hard acid (H^+) – soft base (SH^-) interaction which is against HSAB principle, this reaction proceeds from right to left.

6. Reaction of HgO and HgS with HCl

HgO reacts with HCl to form HgCl_2 and H_2O but HgS does not react with HCl.

Explanation. The reaction of HgO and HgS with HCl can be shown as follows:



In reaction (a), since HgCl_2 (product) is obtained by soft acid [Hg^{2+}] – soft base (Cl^-) interaction and $2\text{H}^+ \text{O}^{2-}$ or H_2O (another product) is obtained by hard acid (H^+) – hard base (O^{2-}) interaction, both the interactions are in accordance with HSAB principle. Thus reaction (a) is feasible, i.e. HgO reacts with HCl and forms HgCl_2 and H_2O .

On the other hand, in reaction (b), since one product (HgCl_2) is obtained by soft acid (Hg^{2+}) – soft base (Cl^-) interaction and the other product (H_2S) is formed by hard acid (H^+) – soft base (S^{2-}) interaction, reaction (b) is not feasible, i.e. HgS does not react with HCl.

7. Order of Stability of Hydrogen Halides, HX (X = F, Cl, Br, I).

In HX molecule, H^+ ion is a *hard acid*. Halide ions (X^-) are *hard bases*. The hardness of halide bases *decreases in the order* $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$. This order shows that F^- ion is the *hardest ion* and I^- ion is the *least hard (i.e. softest)* ion. Hence HF which is a hard acid (H^+) – hard base (F^-) combination is the *most stable*. On the other hand, since HI is a *hard acid* (H^+) – *soft base* (I^-) combination, HI is the *least stable*. Thus, the order of stability of HX molecules is as:



8. Occurrence of Metals in Nature

We know that some metals occur as carbonates, oxides and halides in nature while some metals occur as sulphides in nature. Now:

- (i) Since Mg^{2+} , Ca^{2+} , Mn^{2+} , Al^{3+} , Fe^{3+} , Cr^{3+} , etc. metal ions are *hard acids*, these metal ions prefer to combine with CO_3^{2-} , O^{2-} and X^- (halide) ions which are *hard bases* (*hard acid - hard base interaction*) and thus these metal ions occur as *carbonates, oxides* and *halides* in nature.
- (ii) Since Cu^+ , Ag^+ , Pb^{2+} , Hg^{2+} , Pd^{2+} , etc. metal ions are *soft acids*, these metal ions prefer to combine with S^{2-} ion which is a *soft base* (*soft acid - soft base interaction*) and thus occur as sulphides in nature.
- (iii) Since Ni^{2+} , Fe^{2+} , Zn^{2+} , Pb^{2+} , Co^{2+} , etc. metal ions are *border line acids*, these metal ions occur in nature as *oxides* or *carbonates* (hard bases) as well as sulphides (*soft bases*)

It should be clear from the above discussion that since Mg^{2+} , Ca^{2+} and Al^{3+} cations are *hard acids* and S^{2-} ion is a *soft base*, these cations are never found as sulphides in nature.

9. Poisoning of Metal Catalysts.

There are some metals like Ni, Pt, Pd, Cr, Mo, etc. (*soft acids*) which act as catalysts. These metal catalysts can strongly adsorb on their surface the substances like CO, unsaturated hydrocarbons (olefins, arenes, dienes, alkylalkylenes), phosphine and arsine containing ligands which are *soft bases*. The adsorption of soft bases on the surface of the metal catalysts is called poisoning of the metal catalysts, since the adsorption of the ligands by the metals catalysts blocks the active sites of the metal catalysts. The adsorption of soft bases (*i.e.* poisoning of the metal catalysts) takes place through soft acid (metal catalysts) - soft base (ligands) interaction. Since metal catalysts are soft acids, these are not affected by hard bases or ligands containing N, O or F.

Theoretical Basis of Hardness and Softness of Acids and Bases

Several theories have been put forth to explain the basis of hard acid - hard base and soft acid - soft base interactions. However, no single theory is completely satisfactory. These interactions may be of the following types:

- 1. Hard acid - hard base electrostatic (ionic) interaction.** According to the most accepted view, the hard acid - hard base interaction is an electrostatic (ionic) interaction, *i.e.* the bonding between hard acid and hard base is predominantly ionic. For example, the interaction between hard acids like Li^+ , Na^+ , K^+ , etc. and hard bases like OH^- , F^- , O^{2-} , etc. gives ionic compounds.

Now we know that if both the ions (*i.e.* positive and negative ions) of an ion pair are smaller in size, the inter-nuclear distance between such ions would also be smaller and hence the attraction between such two ions would be greater. Consequently, the compound resulted from hard acid - hard base interaction would be highly stable.

- 2. Soft acid - soft base covalent interaction.** We know that most of the soft acids are transition metal ions which contain 6 to 10 electrons in their *d*-orbitals. These *d*-electrons of the metal ions (soft acids) have polarising power and soft bases like S^{2-} , I^- , etc. are easily polarisable.

As a result, bonding between soft acids and soft bases is largely covalent (Recall covalent bonding is established between Li^+ and I^- ions due to polarisation of I^- ion by Li^+ ion)

3. **π -bonding in soft acid – soft base interaction.** In soft acid – soft base interactions, π -bonding plays an important role. Soft acids are generally metals in low oxidation states and have a tendency to form pi bonds with soft bases. Soft bases are good pi bonding ligands.

Miosons Relation

Miosons and coworkers (1967) have proposed a relation with the help of which we can predict whether a given species is hard or soft. This relationship is:

$$pK = -\log K = aX + bY + C$$

where K = equilibrium constant for the dissociation of metal-ligand (*i.e.* acid-base) complex. X and Y = parameters for the metal ions (acids). These are called *metal or acid parameters*. a and b = parameters for the ligands (*i.e.* bases). These are called *ligand parameters*. C = a constant required to adjust the value of pK in such a way that all of them lie in the same scale.

Values of acid parameter (Y) for some metal ions which may be hard acids as well as soft bases are given below:

Hard acids: $\text{Li}^+ = 0.36$, $\text{Al}^{3+} = 0.70$, $\text{Mg}^{2+} = 0.87$, $\text{Na}^+ = 0.93$, $\text{Ca}^{2+} = 1.62$, $\text{Fe}^{3+} = 2.37$, $\text{Ca}^{2+} = 2.56$, $\text{Cs}^+ = 2.73$, $\text{Co}^{2+} = 2.93$

Soft acids: $\text{Sn}^{2+} = 3.17$, $\text{Tl}^{3+} = 3.2$, $\text{Cu}^+ = 3.45$, $\text{Pb}^{2+} = 3.58$, $\text{Tl}^+ = 3.78$, $\text{Hg}^{2+} = 4.25$, $\text{Au}^+ = 5.95$

If the value of Y is less than 2.8, the acid is hard and if the value of Y is more than 3.2, the acid is soft.

The value of b (ligand parameter) increases as we move from hard bases to soft bases, *i.e.* with the increase in the value of b , the softness of bases increases as shown below.

OH^-	NH_3	Cl^-	⋮	Br^-	I^-	$\text{S}_2\text{O}_3^{2-}$
0.40	1.04	2.49	⋮	5.58	7.17	12.4
Hard bases			⋮	Soft bases		
—————				—————		
				Softness of bases increases		
				—————>		

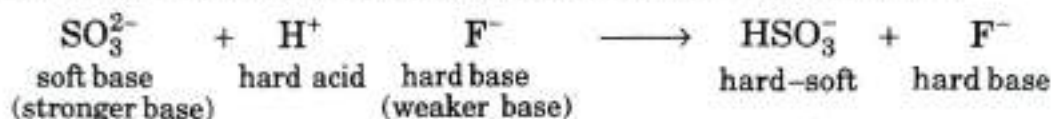
If the value of b is less than 3, the base is hard and if the value of b is more than 5, the base is soft.

Acid-Base Strength and Hardness and Softness

Hardness or softness of an acid or a base has no relationship with acidic strength of an acid and basic strength of a base. For example: (i) OH^- and F^- both are *hard bases* but OH^- ion is much stronger (about 10^{13} times) base than F^- ion. (ii) SO_3^{2-} and Et_3P both are *soft bases* but Et_3P is much stronger (about 10^7 times) than SO_3^{2-} ion towards CH_3Hg^+ which is a *soft acid*. (iii) SO_3^{2-} ion is a stronger base than F^- ion (iv) OH^- ion is much stronger than SO_3^{2-} ion.

There are many reactions which proceed from left to right, but these reactions cannot be explained on the basis of HSAB principle, since in these reactions the products are *not formed* by hard-hard or soft-soft interactions, rather the products are formed either by hard-soft or soft-hard interaction. Such reactions are explained on the basis of relative basic strength of bases involved in these reactions.

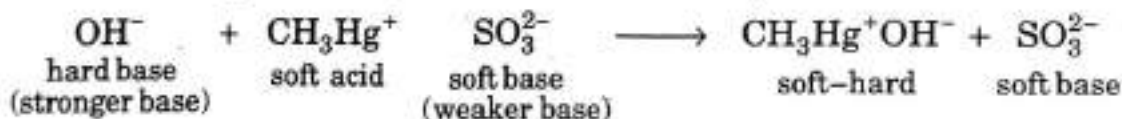
Examples: (i) The following reaction proceeds from left to right.



The formation of HSO_3^- (product) cannot be explained on the basis of HSAB principle, since the product (HSO_3^-) is formed by hard acid (H^+) – soft base (SO_3^{2-}) interaction. According to HSAB principle HSO_3^- (product) should have been formed either by hard acid-hard base or by soft acid-soft base interaction.

How to explain this reaction? The feasibility of the above reaction is explained on the basis of relative basic strength of SO_3^{2-} and F^- bases. Since SO_3^{2-} ion is stronger base than F^- ion, SO_3^{2-} ion displaces F^- ion from HF and forms HSO_3^- which is a hard acid (H^+) – soft base (SO_3^{2-}) – product

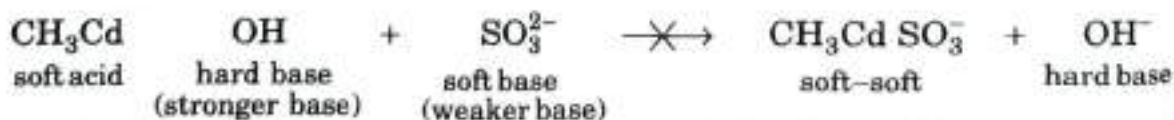
(ii) The following reaction proceeds from left to right.



The formation of CH_3HgOH (product) cannot be explained on the basis of HSAB principle, since the product (CH_3HgOH) is formed by soft acid (CH_3Hg^+) – hard base (OH^-) interaction. According to HSAB principle, CH_3HgOH (product) should have been formed either by hard acid – hard base or by soft acid – soft base interaction.

How to explain this reaction? The feasibility of the above reaction is explained on the basis of relative basic strength of OH^- and SO_3^{2-} bases. Since OH^- ion is stronger base than SO_3^{2-} ion, this ion displaces SO_3^{2-} ion from $\text{CH}_3\text{HgSO}_3^-$ and CH_3HgOH which is a soft acid (CH_3Hg^+) – hard base (OH^-) product.

(iii) The reaction

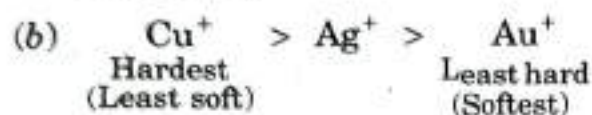
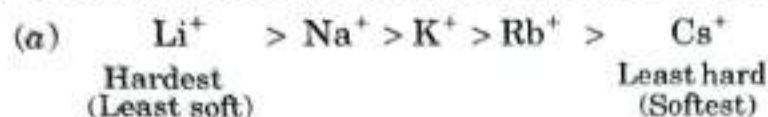


is *not feasible* (i.e. this reaction does not occur in the forward direction), since SO_3^{2-} base is weak base than OH^- ion and hence SO_3^{2-} ion is not able to displace OH^- ion from $\text{CH}_3\text{Cd OH}$ to form $\text{CH}_3\text{Cd SO}_3^-$ (product).

We can conclude from the above discussion that Lewis acid – Lewis base reactions can be explained by two independent principles which depend on (i) softness and hardness of acids and bases, and (ii) acidic strength of acids and basic strength of bases.

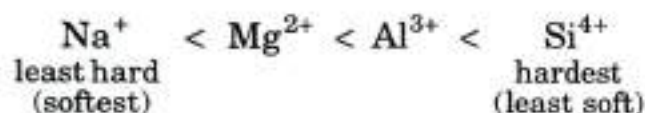
Variation of Hardness and Softness of Cations in a Group

We know that the size of the cations of the elements of a group having the same charge increases with the increase of atomic number. Due to the increase in the size, the hardness of cations decreases and softness increases. For example:



Variation of hardness and softness of cations in a period

When we move from left to right in a period, the charge on cations increases and hence hardness of cations increases. For example:



Thus in a period, alkali metal cations are the softest.

Cations with High Charge are Hard Acids

The cations with high charge like Mn^{7+} , Cr^{6+} , Os^{8+} , Pt^{6+} , I^{7+} , S^{6+} etc. are hard acids. This nature of these cations is confirmed by the fact that these cations combine with hard bases like O^{2-} and F^- and form stable compounds and complex ions. Examples of compounds and complex ions are MnO_4^- , CrO_4^{2-} , OsO_4 , PtF_6 , IF_7 and SF_6 .

Transition Metal Ions in their Low Oxidation States are Soft Acids

Transition metal ions in their low oxidation state act as soft acids and hence combine with soft bases like CO , CNR , PR_3 , etc. to form stable complexes. Examples of some stable complexes are $\text{Ni}(\text{CO})_4$, $\text{Cr}(\text{CO})_6$, $\text{Ni}(\text{CNR})_4$, $\text{Ni}(\text{PCl}_3)_4$, $\text{Fe}(\text{CO})_5$ etc.

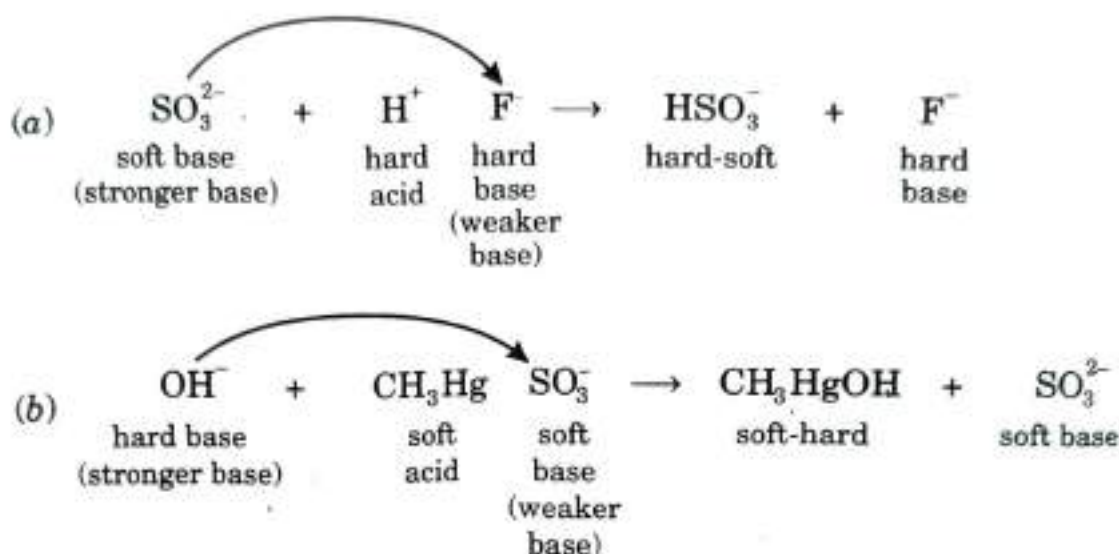
Many Soft Acids are Toxic

Many soft acids are toxic, For example:

- (i) Hg^{2+} and CH_3Hg^+ which are soft acids can bind with cysteine S in enzymes and can thus destroy the enzymatic functions.
- (ii) Pb^{2+} and Cd^{2+} ions which are soft border line acids are quite toxic, since these metal ions react with enzyme-SH groups and thus spoil the enzyme function.

Limitations of HSAB Principle

- (i) HSAB principle is unable to explain the reactions which take place through *hard acid-soft base* and *soft acid-hard base* interactions. For example, consider the following reactions which take place spontaneously in the forward direction.



On the basis of HSAB principle, reaction (a) should not be expected to proceed from left to right, since the formation of HSO_3^- (product) does not take place through soft acid-soft base or hard acid-hard base interaction. The formation of HSO_3^- occurs through hard acid (H^+) and soft base (SO_3^{2-}) combination which is against HSAB principle. The occurrence of this reaction can be explained as follows: SO_3^{2-} ion is a *stronger soft base* and F^- ion is a *weaker hard base* ($\text{SO}_3^{2-} > \text{F}^-$). Being stronger, SO_3^{2-} ion (stronger base) displaces F^- ion (weaker base) from HF to form HSO_3^- .

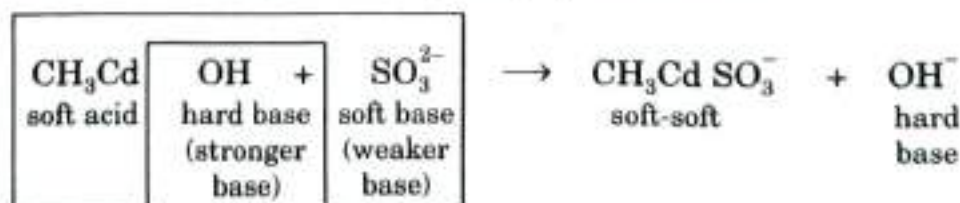
On the basis of HSAB principle, reaction (b) should not proceed from left to right, since the formation of CH_3HgOH (product) does not take place through soft acid-soft base or hard acid-hard base interaction. The formation of CH_3HgOH occurs through soft acid (CH_3Hg^+) – hard base (OH^-) combination which is against HSAB principle. The occurrence of this reaction can be explained as follows:

OH^- ion is a *stronger hard base* and SO_3^{2-} ion is a *weaker soft base* ($\text{OH}^- > \text{SO}_3^{2-}$). Being stronger, OH^- ion (stronger base) displaces SO_3^{2-} ion (weaker base) from $\text{CH}_3\text{HgSO}_3^-$ to form CH_3HgOH .

It should be clear from the above discussion that the relative strength of bases ($\text{SO}_3^{2-} > \text{F}^-$ and $\text{OH}^- > \text{SO}_3^{2-}$) plays an important role in explaining the occurrence of these reactions. HSAB principle cannot be used to explain these reactions.

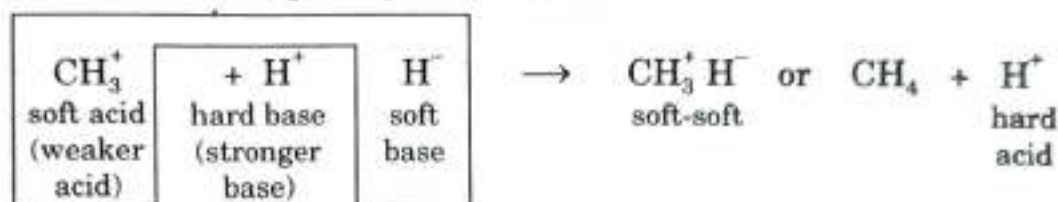
(ii) These are many reaction which, according to HSAB principle, should proceed from left to right. Actually these reactions do not take place in the forward direction.

Examples (a) According to HSAB principle, the reaction:



should proceed from left to right to produce $\text{CH}_3\text{CdSO}_3^-$ as shown above by soft acid (CH_3Cd^+) - soft base (SO_3^{2-}) combination. As a matter of fact this reaction does not occur to give $\text{CH}_3\text{CdSO}_3^-$. The non-occurrence of this reaction is explained on the basis of relative strength of OH^- and SO_3^{2-} bases. Since SO_3^{2-} ion is weaker base than OH^- ion, this ion (i.e., SO_3^{2-} ion) is not able to displace stronger OH^- base from CH_3CdOH to produce $\text{CH}_3\text{CdSO}_3^-$.

(b) According to HSAB principle, the reaction:



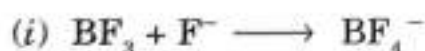
should proceed from left to right to produce CH_4 as shown above by soft acid (CH_3^+) -soft base (H^-) combination. As a matter of fact this reaction does not occur due to its unfavourable entropy change ($= + 359 \text{ kJ /mole}$) to give CH_4 , since CH_3^+ is a weaker acid than H^+ and hence is not able to displace stronger H^+ acid from $\text{H}^+ \text{H}^-$ to produce CH_4 .

Symbiosis

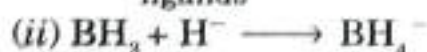
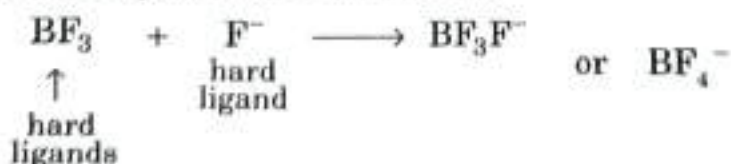
The term symbiosis was introduced by Jorgenson in 1868.

According to Jorgenson, soft ligands have a tendency to combine with a centre (metal ion) which is already linked with soft ligands. Similarly hard ligands have a tendency to combine with a centre which is already associated with hard ligands. Thus the term symbiosis indicates the tendency of ligands to combine with a centre (metal ion) which is already linked with ligands.

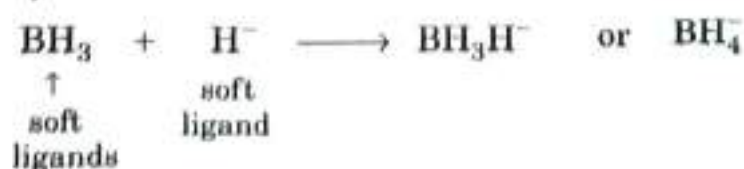
Examples: Let us consider the following reactions:



In BF_3 molecule, B-atom is associated with three hard ligands (F^- ions). Due to symbiosis tendency of F^- ion (hard ligand), this ligand (i.e. F^- ion) prefers to combine with F^- ions (hard ligands) present in BF_3 and thus forms BF_4^- ion. Thus the formation of BF_4^- ion can be shown as:

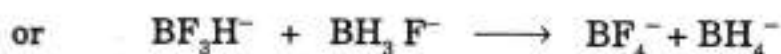
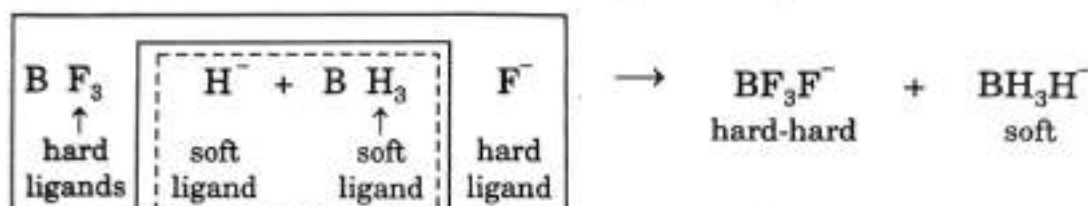


Since H-atoms present in BH_3 molecule are soft ligands and H^- ion is also a soft ligand, BH_4^- ion is formed

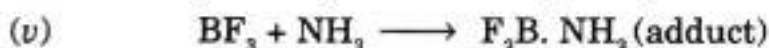
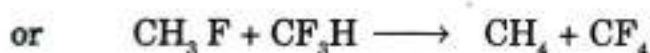
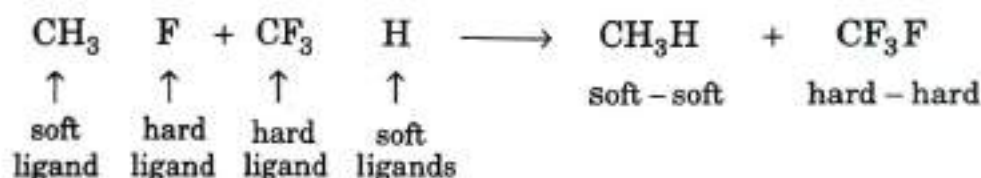




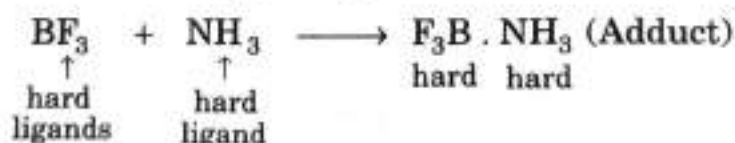
In BF_3 , B-atom is linked with three hard ligands (F^- ions) and H^- present in BF_3H^- is a soft ligand. In BH_3 , B-atom is linked with three soft ligands (H-atoms) and F^- ion present in BH_3F^- is a hard ligand. In this reaction, F^- ion (hard ligand) present in BH_3F^- prefers to combine with B-atom of BF_3 which is already linked with F-atoms (hard ligands) to form BF_4^- . Similarly H^- ion (soft ligand) present in BF_3H^- prefers to combine with B-atom of BH_3 which is already associated with H-atom (soft ligand). Thus, the formation of BF_4^- and BH_4^- ions can be shown as:



(iv) Fluorinated methanes (CH_3F and CF_3H) react in the same way as BF_3H^- and BH_3F^- react together as shown above:



In BF_3 molecule, B-atom is associated with three hard ligands (F atoms) and NH_3 molecule is also a hard ligand. Hence, NH_3 (hard ligand) gets associated with B-atom of BF_3 molecule to form $\text{F}_3\text{B} \cdot \text{NH}_3$ adduct.



Relation of Electronegativity (EN) of Acids and Bases with Their Hardness and Softness

Hardness and softness of acids and bases are related with their EN values. In general, a species having high EN is hard and the species with low EN value is soft. For example since Li^+ , Na^+ , etc. ions have high EN, these ions are hard acids. On the other hand, since transition metal ions in low oxidation states like Cu^+ , Ag^+ , Au^+ , etc. have low EN, those ions are soft acids. On similar basis the hardness and softness of bases can also be explained.

The relationship between hardness/softness of acids and bases and their EN values helps us to explain the fact that CF_3 group is harder than CH_3 group and BF_3 molecule is harder than BH_3 molecule. This is because the presence of highly electronegative groups makes the central atom more electronegative.