

US03CCHE21 (Inorganic Chemistry)

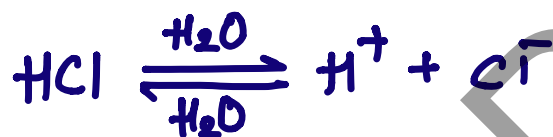
Unit-1 Acids and Bases

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Following are the important modern concept of acids and bases :

1. ARRHENIUS CONCEPT (1884) -THE WATER ION SYSTEM:

According to this concept, any substance contains hydrogen which gives H^+ ions in aqueous solution is acid, and a base which gives OH^- ions in aqueous solution. Thus HCl is an acid and NaOH is a base. And the neutralisation process can be represented by:



Utility:

(i) Since the reaction representing the naturalization process involves the combination of H^+ and OH^- ions. 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) Neutralization, salt hydrolysis, acid-base strength also explain by this theory.

Limitations:

(i) 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.

(ii) It cannot account for the acidic and basic character of 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.

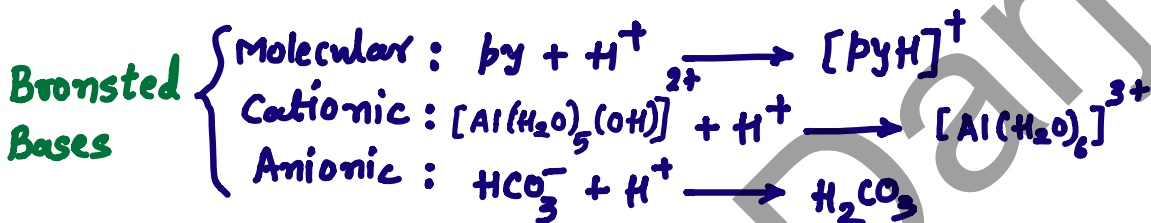
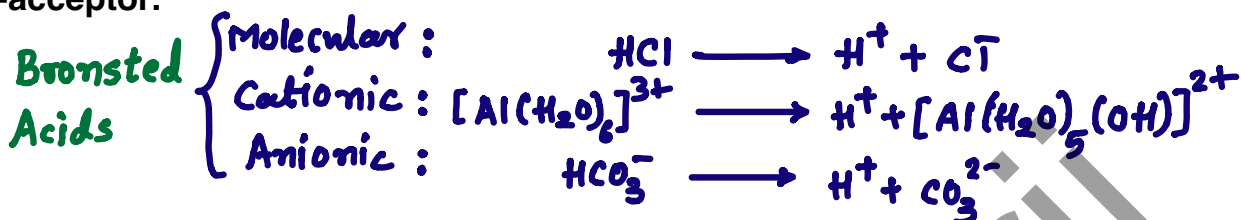
(iii) The neutralisation process is limited to those reactions which can occur in aqueous solution only, although reactions involving salt formation do occur in many other solvents and even in the absence of solvents.

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

(v) CaO, NH_3, Na_2CO_3 are bases but do not contain OH^- & CO_2, SO_2, SO_3 are acids but do not contain H^+ .

2. Bronsted-Lowry Theory - The Proton-Donor-Acceptor system:

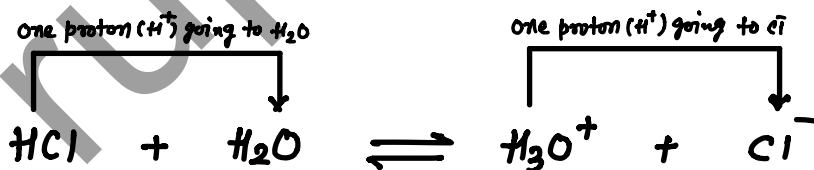
According to this theory, an acid is defined as any hydrogen containing material (a molecule or a cation or an anion) that can release a proton (H^+) to any other substance, whereas a base is any substance (a molecule or a cation or an anion) that can accept a proton from any other substance. In short, **an acid is a proton-donor and a base is a proton-acceptor.**



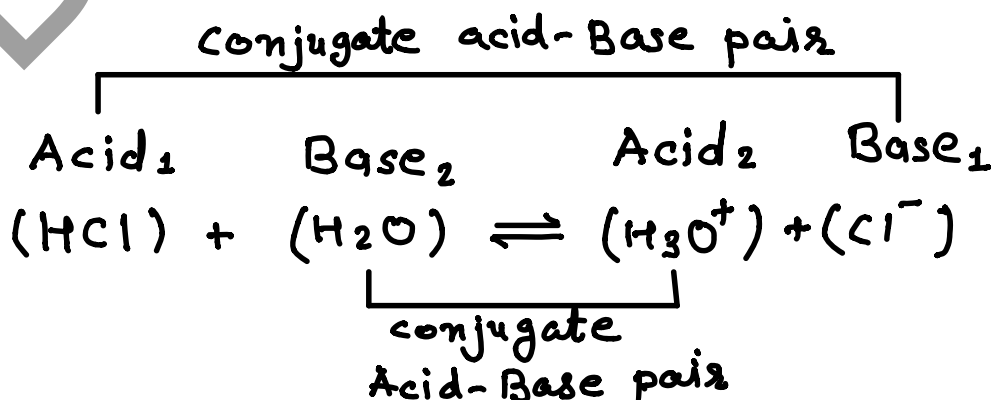
Conjugate Acid-Base Pairs :

In forward reaction HCL is an acid since it donates a proton to H_2O and water accepts a proton from HCL therefore H_2O is a base. In the reverse reaction H_3O^+ is an acid and Cl^- is a base. The members of which can be formed from each other mutually by the gain or loss of proton are called **conjugate acid-base pairs.**

consider a reaction:



Thus on the basis of this concept $Acid_1$ and $Base_1$ form one conjugate acid-base pair and $Acid_2$ and $Base_2$ form another conjugate acid-base pair.



Acid		Conjugate Base	
Name (In the order of decreasing strength as an acid i.e., K_a decreasing)	Formula	Formula	Name (In the order of increasing strength as a base i.e., K_b increasing)
Perchloric acid (Strongest acid)	HClO_4	ClO_4^-	Perchlorate ion (Weakest base)
Sulphuric acid	H_2SO_4	HSO_4^-	Hydrogen sulphate ion
Hydrogen chloride	HCl	Cl^-	Chloride ion
Nitric acid	HNO_3	NO_3^-	Nitrate ion
Hydronium ion	H_3O^+	H_2O	Water
Hydrogen sulphate ion	HSO_4^-	SO_4^{2-}	Sulphate ion
Phosphoric acid	H_3PO_4	H_2PO_4^-	Dihydrogen phosphata ion
Acetic acid	CH_3COOH	CH_3COO^-	Acetate ion
Hexa aquo aluminium (III) ion	$[\text{Al}(\text{H}_2\text{O})_6]^{3+}$	$[\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$	Hydroxo penta aquo aluminium (III) ion
Carbonic acid	H_2CO_3	HCO_3^-	Hydrogen carbonate ion
Hydrogen sulphide	H_2S	HS^-	Hydro sulphide ion
Ammonium ion	NH_4^+	NH_3	Ammonia
Hydrogen cyanide	HCN	CN^-	Cyanide ion
Hydrogen carbonate ion	HCO_3^-	CO_3^{2-}	Carbonate ion
Phenol	$\text{C}_6\text{H}_5\text{OH}$	$\text{C}_6\text{H}_5\text{O}^-$	Phenoxide ion
Water	H_2O	OH^-	Hydroxide ion
Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$	$\text{C}_2\text{H}_5\text{O}^-$	Ethoxide ion
Ammonia	NH_3	NH_2^-	Amide ion
Methyl amine	CH_3NH_2	CH_3NH^-	Methyl amide ion
Hydrogen	H_2	H^-	Hydride ion
Methane (Weakest acid)	CH_4	CH_3^-	Methide ion (Strongest base)

Table: Acid-Base chart containing some common conjugate acid-base pairs

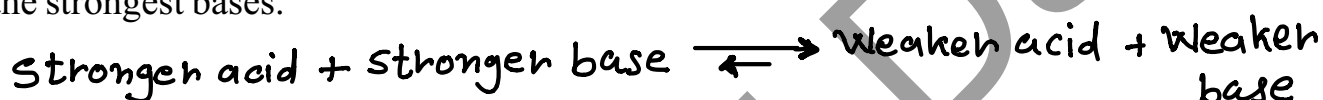
Two important axioms of the Bronsted concept and position of equilibrium in acid-base reactions:

Let us consider the reaction: $\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-$



In the equilibrium mixture two acids HCl and H_3O^+ ion are competing to donate protons to a base. stronger Since HCl wins, it is the ^{stronger} acid. Similarly two bases, H_2O and Cl^- ion, are competing to accept protons. Here H_2O is the stronger base. It will be seen that the stronger acid, HCl, has the weaker conjugate base, Cl^- ion and the stronger base, H_2O , has weaker conjugate acid, H_3O^+ ion.

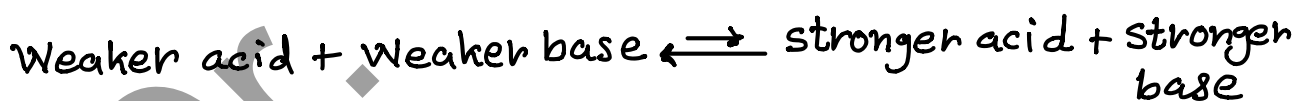
The stronger acid and weaker base form one conjugate acid-base pair and weaker acid and strong base form another conjugate acid base pair. From the above table HClO_4 is the strongest acid, its conjugate base ClO_4^- ion, is consequently the weakest base. CH_4 and H_2 are the weakest acids, their conjugate bases, CH_3^- ion and H^- ion respectively, are the strongest bases.



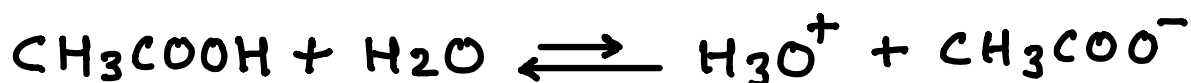
As a stronger acid, HCl is highly ionised. At equilibrium, the above reaction proceeds far to the right, with most of HCl ionised to form H_3O^+ and Cl^- ions. This fact can be illustrated by using arrows of unequal length to designate the forward and reverse reactions respectively.



The longer arrow indicates that the position of equilibrium lies to the right. In the ionisation of CH_3COOH in H_2O , equilibrium is reached when the reaction has proceeded to the right only to a slight extent.



Here the longer arrow indicates that the position of equilibrium lies to the left. Evidently H_3O^+ ion in equilibrium (2) is stronger acid and CH_3COO^- ion is a stronger base. It is also evident that the stronger acid H_3O^+ ion has the weaker conjugate base, H_2O and the stronger base, CH_3COO^- has the weaker conjugate acid, CH_3COOH .

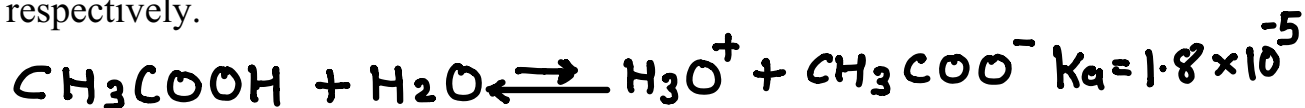


Relative Strengths of Acids and Bases:

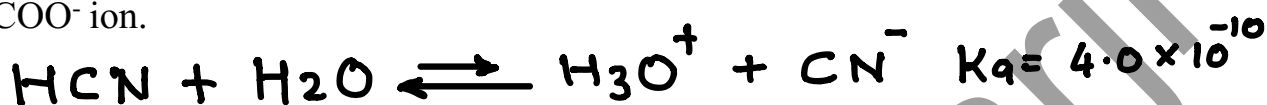
According to the Bronsted concept, a strong acid has a strong tendency to donate a proton and a strong base has a strong tendency to accept a proton. At least two general

methods are generally used for the comparison of relative acidity of given acids.

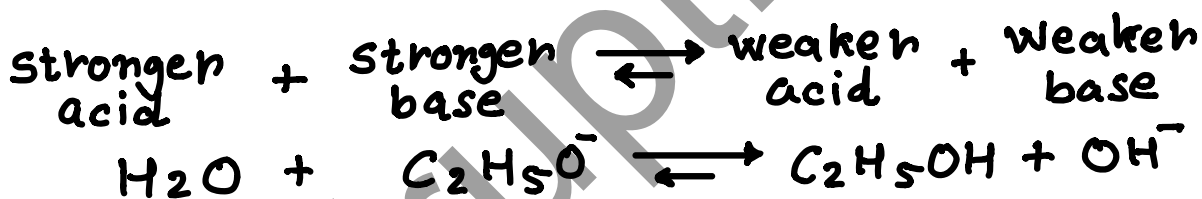
(i) The first method consists of making a comparison of proton-donating tendencies of different acids towards the same base H_2O . Suppose we have to compare the acidic strengths of CH_3COOH and HCN . Experimentally it has been observed that the ionisation acidity constant, K_a , for CH_3COOH and HCN at 25° is 1.8×10^{-5} and 4.0×10^{-10} respectively.



CH_3COOH is, therefore, a stronger acid than HCN and CN^- ion is a stronger base than CH_3COO^- ion.



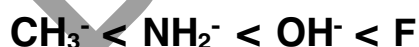
(ii) **Competitive protolysis method:** In this method one acid is added to the conjugate base of another and the equilibrium concentrations are determined experimentally. For example, when H_2O is a stronger acid of conjugate base OH^- is added to stronger base $\text{C}_2\text{H}_5\text{O}^-$ (NaOC_2H_5) of conjugate acid $\text{C}_2\text{H}_5\text{OH}$, it is seen that $\text{C}_2\text{H}_5\text{OH}$ and OH^- form completely. $\text{C}_2\text{H}_5\text{O}^-$ ion is a stronger base than OH^- and H_2O is a stronger acid than $\text{C}_2\text{H}_5\text{OH}$.



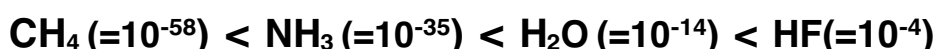
Periodic variation of acidic and basic properties:

(A) Hydracid of the elements of the same period:

We can consider the hydracids of the elements of 2nd period viz. CH_4 , NH_3 , H_2O and HF . These hydrides become increasingly acidic as we move from CH_4 to HF . It is due to the fact that as we move from CH_4 to HF , the stability of their conjugate base viz. CH_3^- , NH_2^- , OH^- and F^- increase in order:



The increase in acidic properties is supported by the successive increase in the dissociation constant values of these hydrides as shown:



(B) Hydracides of the elements of the same group:

(i) Hydracids of VA group elements (NH_3 , PH_3 , AsH_3 , SbH_3 , BiH_3):

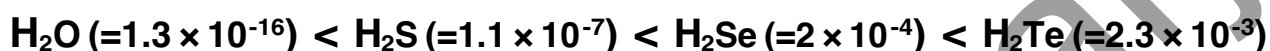
All these hydrides show basic character. With the increase in size and decrease in electronegativity from N to Bi. there is a decrease in electron density in sp hybrid orbital and thus electron donor capacity (ie, basic character) decreases.

(ii) Hydracids of VI A group elements (H₂O, H₂S, H₂Se, H₂Te):

Aqueous solution of the hydrides of this group behave as weak diprotic acids and ionise as : $H_2R \rightleftharpoons H^+ + HR^-$ $HR^- \rightleftharpoons H^+ + R^{2-}$

Acid strength increase in the order : **H₂O < H₂S < H₂Se < H₂Te**

This order is supported by the successive increase of their dissociation constants as shown:



The increasing acidic character reflects decreasing trend in the electron donor ability of OH⁻, HS⁻, HSe⁻ or HTe⁻ ions. The increasing acidic character is explained by saying that as the charge density on the conjugate base decreases from OH⁻ to HTe⁻, the proton is less tightly held in higher members and therefore, acidic character increases.

(iii) Hydracids of VIIA group elements (HF, HCl, HBr, HI) :

The aqueous solutions of these hydrides show acidic character which increases in the order: **HF < HCl < HBr < HI**

This order is explained by: As we pass from HF to HI, there is a gradual decrease in the bond energies. This increases the tendency of HX molecules to split up into H⁺ and X⁻ ions in aqueous solution and thus the acidic character increases from HF to HI.

(C) Oxyacids:

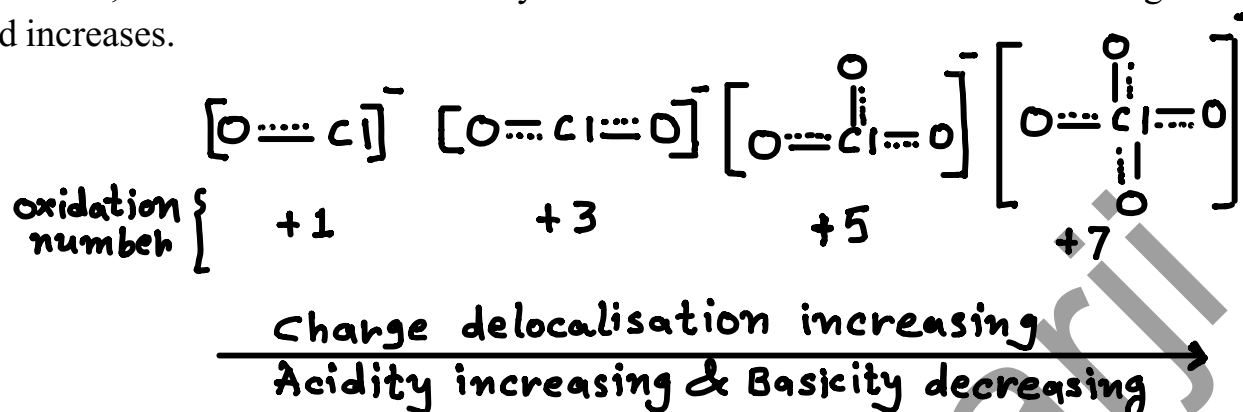
(i) “The acidic character of oxyacids of the same element which is in different oxidation states increases with the increase of its oxidation state”. This is called **oxidation number or oxidation state rule.**

Example : (a) HCl¹⁺O < HCl³⁺O₂ < HCl⁵⁺O₃ < HCl⁷⁺O₄

(b) H₂S⁴⁺O₃ < H₂S⁶⁺O₄ (c) HN³⁺O₂ < HN⁵⁺O₃

Explanation: According to the oxidation rule of oxyacid of halogen that the stronger the acid, the weaker will be its conjugate base and vice versa. For the first series the

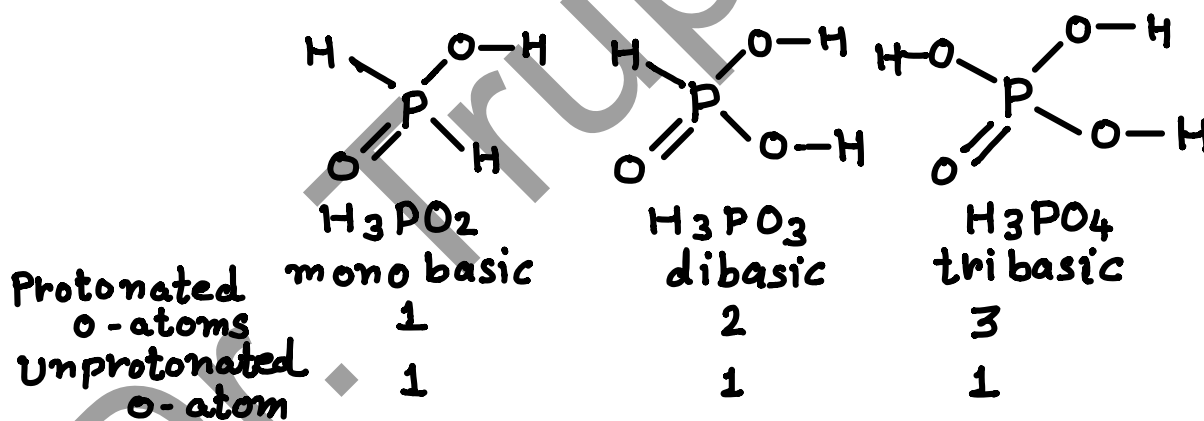
conjugate bases of the acids are : ClO^- , ClO_2^- , ClO_3^- respectively. In these oxyanions the central atom (ie.chlorine) has larger oxidation number has the larger number of lone oxygen atoms for participation in extension of π -bond. Thereby the charge on the ion is delocalised which greatly stabilises the ion and thus decreases its tendency to accept proton i.e., causes the ion to be a very weak base with the result that the strength of the acid increases.



(ii) According to oxidation state rules expected acidic character of oxyacids of phosphorus should be in order : $\text{H}_3\text{P}^+\text{O}_2 < \text{H}_3\text{P}^{3+} < \text{H}_3\text{P}^{5+}\text{O}_4$

But experiment suggest the reverse order : $\text{H}_3\text{PO}_2 \geq \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_4$

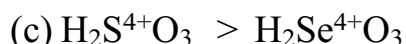
Explanation: The structures of these oxyacids as given below. The oxygen atom attached with a proton is called protonated oxygen while that attached directly with phosphorus (central atom) is known as unprotonated oxygen.



The proton attached to an oxygen atom has a far greater chance of dissociation than that linked directly with is the P central atom. Thus in this series, since the number of protonated oxygen atoms and consequently the number of dissociable protons increases from $\text{H}_3\text{PO}_2 \rightarrow \text{H}_3\text{PO}_3 \rightarrow \text{H}_3\text{PO}_4$. The acidic character of these acids decreases in the order : $\text{H}_3\text{PO}_2 \geq \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_4$

(iii) The acidic character of the oxyacids of different elements which are in the same oxidation state decreases with the increase in the atomic number of the central atom. The following series follow this rule.

Example : (a) $\text{HOCl}^{3+} > \text{HOBr}^{3+} > \text{HOI}^{3+}$ (b) $\text{HCl}^{7+}\text{O}_4 > \text{HI}^{7+}\text{O}_4$



Explanation: As the atomic number of the central atom increases, its electronegativity decreases and its size increases. As a result of this the tendency of the acid to lose a proton to water decreases. This makes the acid a weaker acid.

(D) Hydrated metal ions:

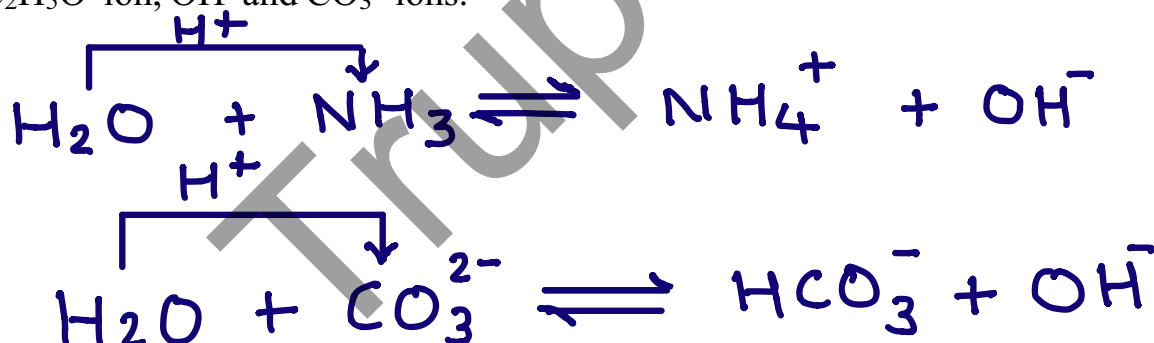
Under favourable conditions one or more protons may dissociate from the coordinated aquo groups. Thus hydrated metal ions also develop acidity.



Acidity increases with the increase of positive charge and basicity increases with the increase of negative charge. Thus $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion is a stronger acid than $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ion and $[\text{Ni}(\text{OH})_4]^{2-}$ is a stronger base than $[\text{Ni}(\text{OH})_4]^-$ ion.

Amphiprotic substances:

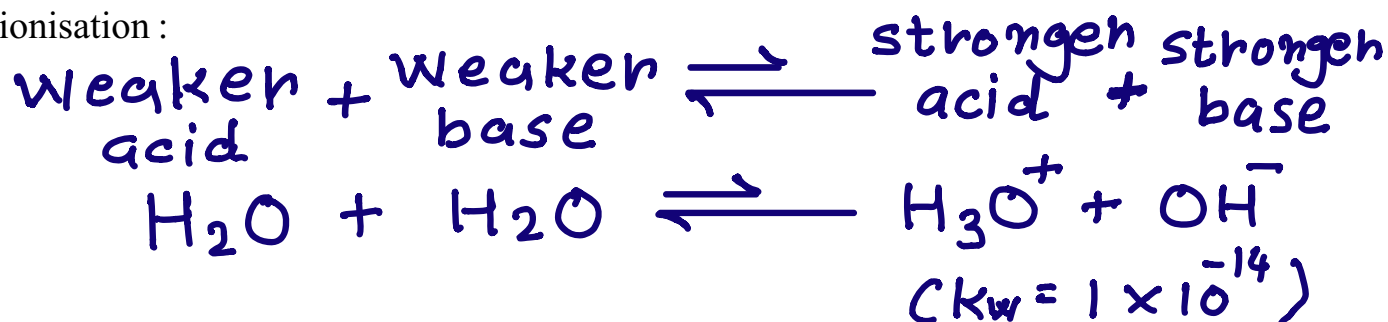
H_2O can act as an acid in the presence of bases stronger than itself such as NH_3 , amine, $\text{C}_2\text{H}_5\text{O}^-$ ion, OH^- and CO_3^{2-} ions.



Water can act as a base in the presence of acids stronger than itself such as HClO_4 , HCl , CH_3COOH and phenol.



Amphiprotic nature of H_2O is well illustrated by extremely slight dissociation or self-ionisation :



The levelling effect, levelling and differentiating solvents :

The apparent strength of a protonic acid is dependent on the solvent in which the acid is dissolved. When all the acids in the acid chart (Table:1) which are stronger than H_3O^+ ion such as HClO_4 , H_2SO_4 , HCl , and HNO_3 are added to H_2O , they donate a proton to H_2O to form H_3O^+ ion and appear to have equal strength, since all these acids are levelled to the strength of H_3O^+ ion which is left in solution and is common to all such solutions. This phenomenon “The strength of all the acids becomes equal to that of H_3O^+ ion is called the **levelling effect** of the solvent, water. Here **water** is called a levelling solvent for all these acids.

In aqueous solution all very strong bases like NaH , NaNH_2 , NaOC_2H_5 are levelled to the strength of OH^- ions, they react completely with H_2O to produce OH^- ions.

The solvent in which complete proton-transfer occurs is called levelling solvent. In other words, the solvent in which the solute is ~100% ionised, are called levelling solvents. Since HF and HCl both are ~100% ionised in liquid NH_3 to give ~100% NH_4^+ ions, these appear to be of equal strength and liq. NH_3 acts as levelling solvent for HF and HCl . In H_2O , HF is only partially ionised, whereas HCl and HBr are ~100% ionised. Thus H_2O is a differentiating solvent for HF , but levelling solvent for HCl and HBr .

Several mineral acids are partially ionised in glacial CH_3COOH medium because CH_3COOH is a poor proton-acceptor but rather a better proton donor. CH_3COOH , therefore, acts as a differentiating solvent towards the mineral acids. But, for bases, CH_3COOH acts as a levelling solvent.

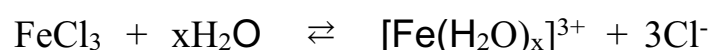
Utility of Bronsted Concept:

(i) It defines acids and bases in terms of the substances themselves and not in terms of their ions in aqueous solution. Thus HCl is an acid because it gives a H^+ ion.

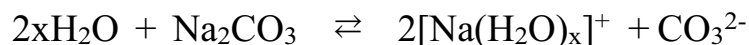


(ii) This concept recognises that acid-base behaviour is neither restricted to, nor depends on, any particular solvent.

(iii) This concept is useful in accounting for the hydrolysis of salt solution. e.g. aqueous solution of FeCl_3 is acidic, since the proton-donor ability of the hydrated ferric ion, $[\text{Fe}(\text{H}_2\text{O})_x]^{3+}$ exceeds the proton-acceptor ability of Cl^- ion and a considerable excess of H_3O^+ ion is produced in this solution, making FeCl_3 acidic.

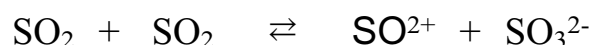


Aqueous solution of a Na_2CO_3 is alkaline in character, because the proton acceptor ability of CO_3^{2-} ion exceeds the proton-donor ability of hydrated sodium ion, $[\text{Na}(\text{H}_2\text{O})^x]^+$.



Limitations:

(i) This concept lays excessive emphasis on the proton-transfer. There are many acids which are protonic in nature. No proton transfer takes place in many acid-base reactions. E.g.,

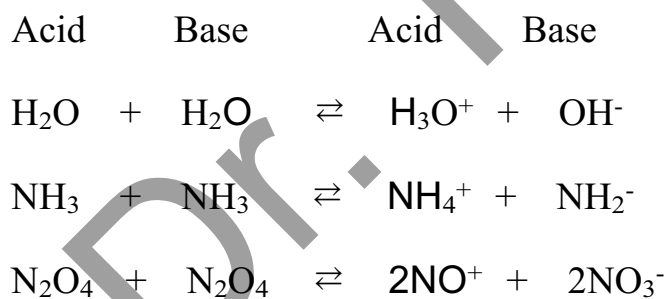


(ii) This concept can not be used to explain acid-base reaction occurring in non protonic solvent such as SO_2 , COCl_2 , N_2O_4 and BrF_3 .

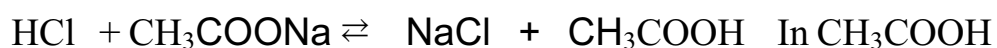
3. GENERAL THEORY OF SOLVENT SYSTEM:

Bronsted concepts can be extended to the reactions occurring in non-aqueous solvents containing hydrogen such as NH_3 , N_3H_4 , HF , H_3SO_4 , CH_3COOH , HCN , and alcohols by Cady and Elsey (1928).

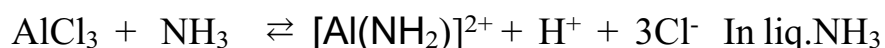
According to him an acid is a solute that, either by direct dissociation or by reaction with the solvent gives the anion characteristic of the solvent and a base is a solute that, either by direct dissociation or by reaction with the solvent, gives the cation characteristic of the solvent.

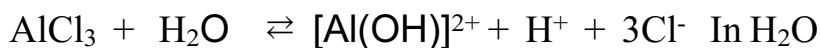


Neutralisation reaction in some non-aqueous solvent are given :

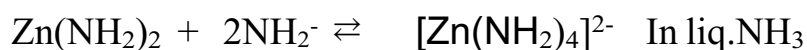


Solvolytic behavior :





Amphoteric behavior :



Utility: This concept of solvent system can be used to explain the acid-base reactions occurring in aqueous and non-aqueous solvents (protonic and non-protonic both)

Limitations:

(i) This theory does not consider a number of acid-base reactions included in the protonic definition.

(ii) It does not explain the acid-base reactions occur in the absence of solvent.

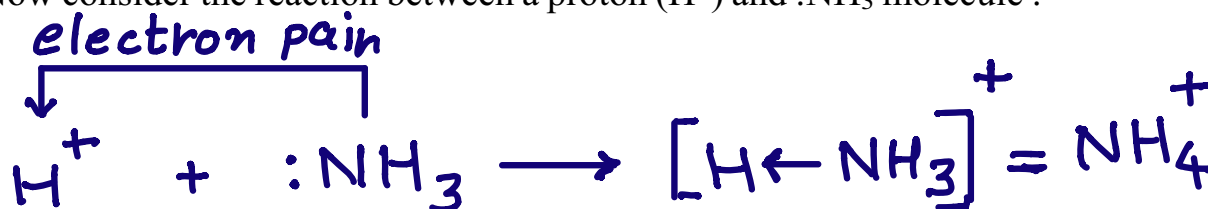
(iii) cannot explain the neutralisation reactions occurring without the presence of ions. Thus this theory can simply be said to be an extension of the Arrhenius water-ion system.

4. THE LEWIS CONCEPT-THE ELECTRON-DONOR-ACCEPTOR SYSTEM:

Theory explains the acid-base phenomena not in terms of ionic reactions but in terms of electronic structure of the acid and base along with the formation of a coordinate covalent bond. According to Lewis (1923), an acid is any species (molecule, radical or ion) that can accept an electron-pair to form a coordinate covalent bond and a base is any species that can donate an electron-pair to the formation of a coordinate covalent bond. Thus, in the Lewis system, **an acid is an electron pair-acceptor and a base is an electron pair donor.**

Thus according to Lewis theory, the process of neutralisation is simply the formation of a coordinate bond between an acid and a base. The product is termed as complex or adduct.

Now consider the reaction between a proton (H^+) and $:\text{NH}_3$ molecule :



In the above reaction proton accepts one electron pair from :NH_3 molecule and is, therefore, Lewis acid, whereas :NH_3 molecule donates an electron pair, is therefore Lewis base. It also accepts proton, is therefore Bronsted base. The adduct is NH_4^+ ion.

Lewis bases and Bronsted-Lowry bases are the same substances, since any molecule or ion which accepts protons does so because of the presence of an unshared pair of electrons.

Bronsted and Lewis theories are thus identical as far as bases are concerned except that the wording used for definition of the bases is different in both theories. Thus NH_3 , H_2O , OH^- , Cl^- , CN^- etc. are the bases on the Bronsted as well as on the Lewis systems.

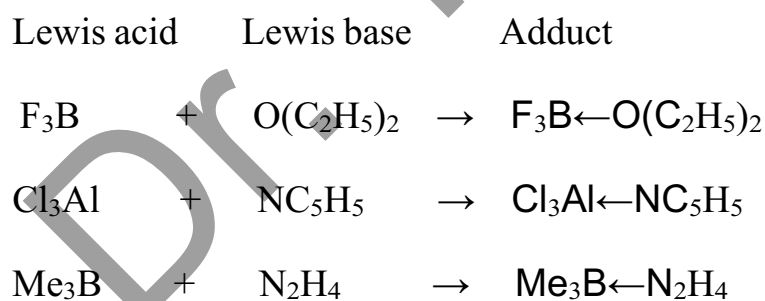
But few compounds such as amides, ethers, nitriles, C_2H_4 , C_2H_2 , C_6H_6 , etc. which have little or no tendency to accept protons but react readily with Lewis-acids and are therefore Lewis bases. Thus all Bronsted bases may be Lewis bases but all the Lewis bases may not be Bronsted bases.

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. They are classified as:

(i) Molecules containing a central atom with an incomplete octet:

Typical examples of this class of acids are electron deficient molecules such as alkyls and halides of Be, B and Al. Examples are shown below :



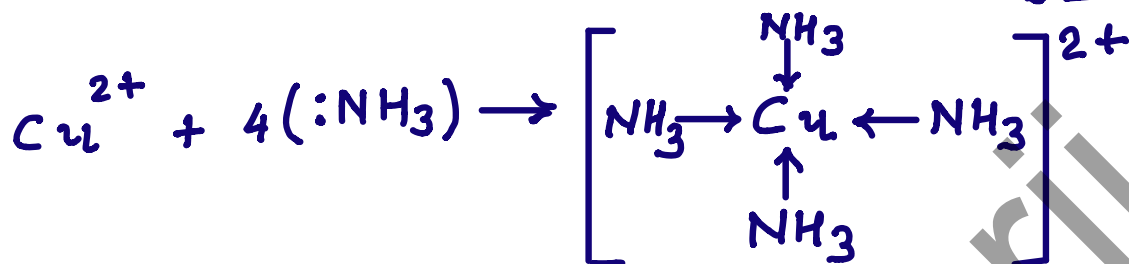
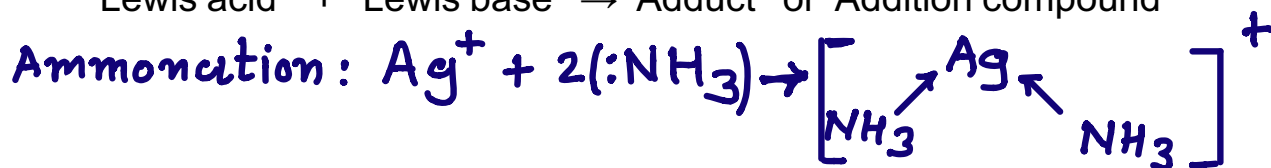
(ii) Molecules containing a central atom with vacant d-orbitals.

The central atom of the halides such as SiX_4 , GeX_4 , TiX_4 , SnX_4 , PX_3 , PCl_5 , SF_4 , TeCl_4 , etc. have vacant d-orbitals therefore, accept an electron pair from the Lewis base to accommodate in their vacant d-orbital. These substances vigorously hydrolysed by H_2O to form an oxy acid or oxide of the central atom.

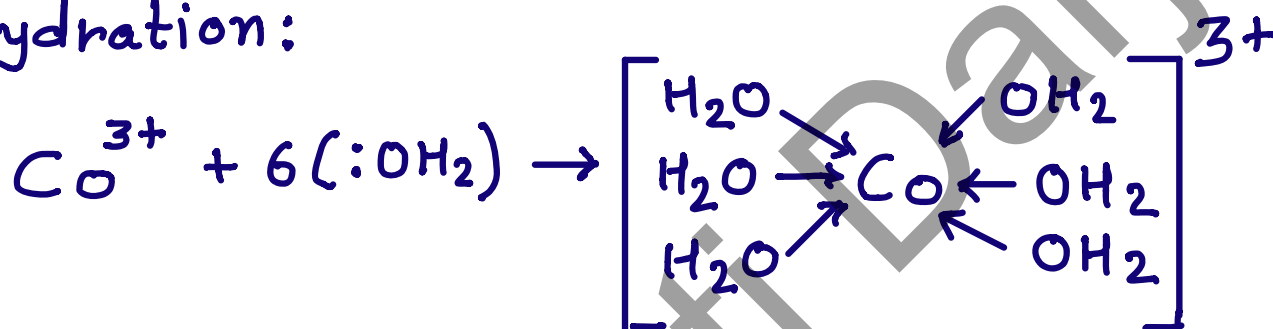
(iii) Simple cations:

Theoretically all simple cations are potential Lewis acids. Reactions of some cations as Lewis acids with Lewis Bases are shown below.

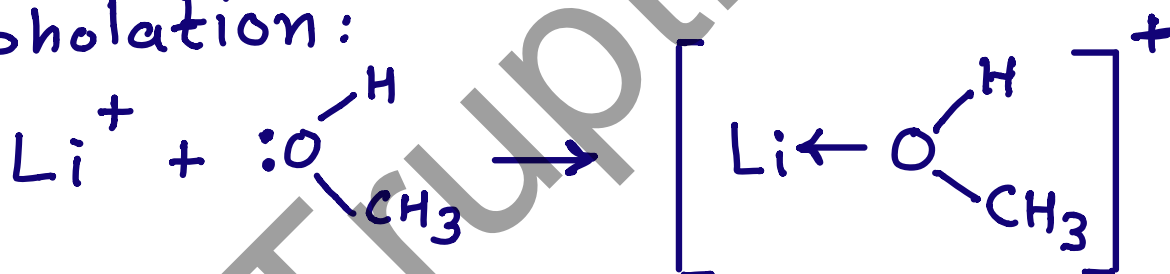
Lewis acid + Lewis base \rightarrow Adduct or Addition compound



Hydration:



Alcoholation:



The Lewis acid strength of the simple cations increases with :

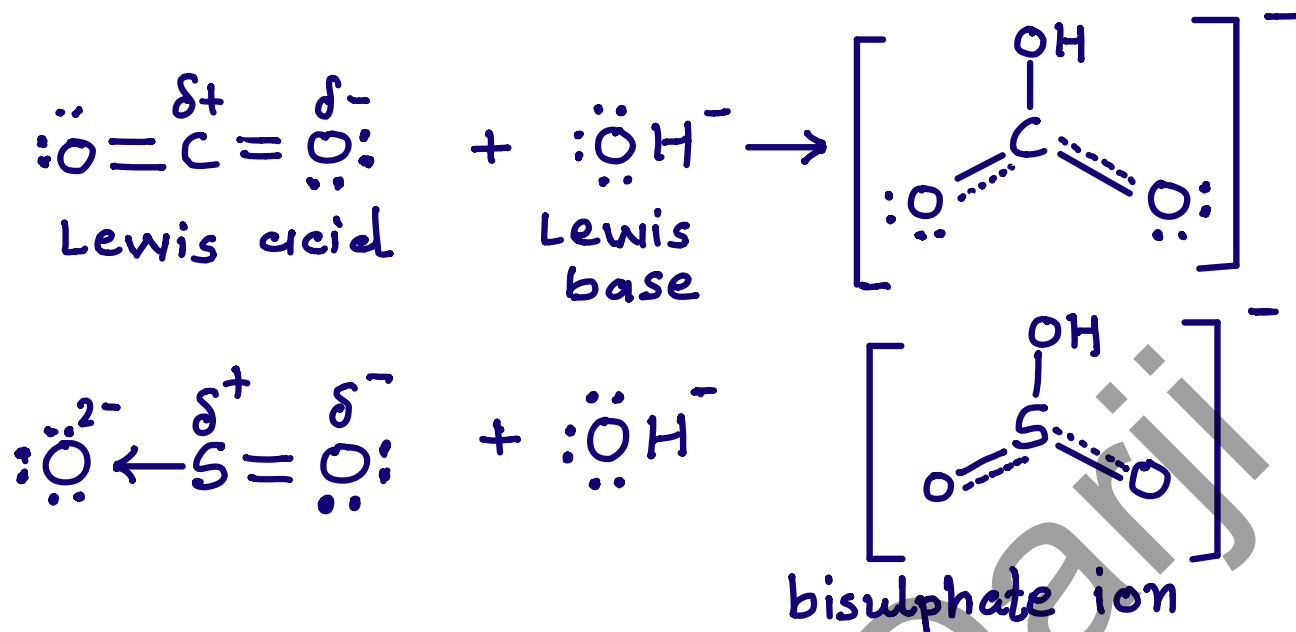
- (a) An increase in the positive charge carried by the cation
- (b) An increase in the nuclear charge of atoms in the same period of the periodic table.
- (c) A decrease in ionic radius.
- (d) a decrease in the number of shielding electrons.

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 tables.

(iv) Molecule having multiple bonds between atoms of dissimilar electronegativity

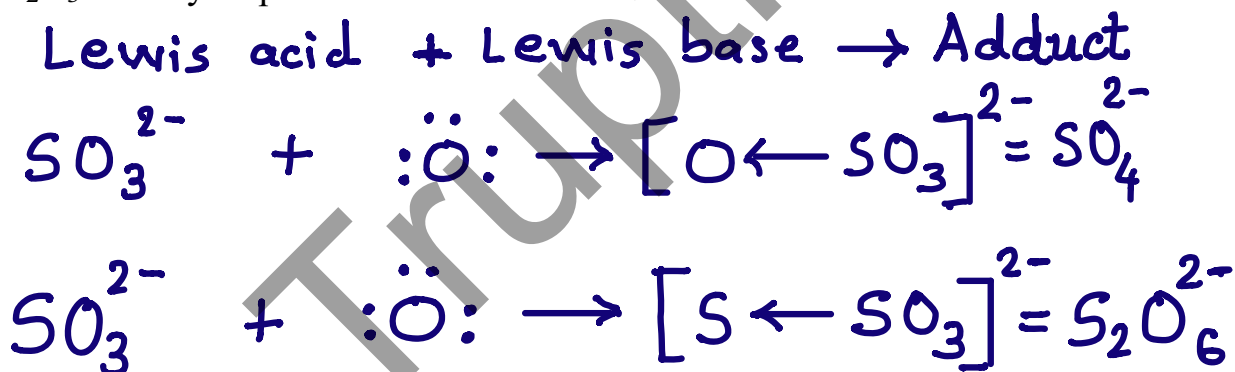
Typical examples of Lewis acids are CO_2 , SO_2 , and SO_3 . In these compounds the oxygen atoms are more electronegative than S or C- atoms. As a result, electron density is displaced away from carbon or sulphur atoms towards the O-atom, making

the C- or S-atom electron deficient. Therefore they are able to accept an electron pair from a Lewis base such as OH⁻ ions to form dative bonds.



(v) Elements with an electron sextant :

Oxygen and sulphur atoms contain six electrons in their valence shell and can, therefore, be regarded as Lewis acids. The oxidation of SO₃²⁻ to SO₄²⁻ ion by oxygen and to S₂O₃²⁻ ion by sulphur are the acid-base reactions.



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 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) Explains the long accepted basic properties of metallic oxides and acidic properties of non-metallic oxides.

(iv) This theory includes reactions occurring in the gas phase, at high temperature and in non aqueous-solvent.

(v) Lewis concept is of great value in cases Where the protonic concept is inapplicable, for example, in reaction between acidic and basic oxides in the fused state.

Limitation :

(i) Since the strength of Lewis acids and bases is found to depend on the type of reaction, so it is not possible to arrange them in any order of their relative strength. Thus, for example, fluoride complex of Be^{2+} ion is more stable than that of Cu^{2+} ion, indicating that Be^{2+} ion is more acidic than Cu^{2+} ion. On the other hand amine complex of Cu^{2+} is more stable than that of Be^{2+} ion indicating that Cu^{2+} is more acidic than Be^{2+} ion.

(ii) According to the criteria, an acid-base reaction should be a rapid reaction. There are, however, many Lewis acid-base reactions which are slow.

Classification of Lewis Acids and Bases into Hard and Soft Acids and Bases :

Soft and Hard Bases: Soft Lewis bases are those in which the donor atoms are easily polarised and have low electronegativity. Hard Lewis bases are those in which the donor atoms have low polarizability and high electronegativities Table contains some typical bases which are classified as hard, intermediate and soft bases. Softness of the Lewis bases increases with the increase in the size of the donor atom. Thus, among the halide ions, softness increases in the order: (Hardest base) $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$ (Softest base).

Table: Classification of Lewis bases and Lewis acids :

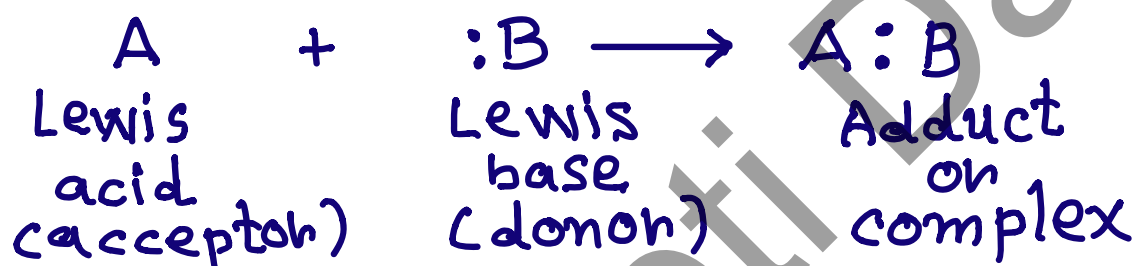
Hard bases	Borderline or intermediate bases	Soft bases
H_2O , OH^- , F^- , CH_3COO^- , PO_4^{3-} , SO_4^{2-} , Cl^- , CO_3^{2-} , ClO_4^- , NO_3^- , ROH , RO^- , NH_3 , RNH_2 , N_2H_4	$\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_5\text{H}_5\text{N}$, Br^- , NO_2^- , SO_3^{2-} , N_2	R_4S , RSH , I^- , SCN^- , $\text{S}_2\text{O}_3^{2-}$, R_3P , R_3As , $(\text{RO})_3\text{P}$, CN^- , RNC , CO , C_2H_4 , C_6H_6 , H^-
Hard acids	Borderline or intermediate acids	Soft acids
H^+ , Li^+ , Na^+ , K^+ , Be^{2+} , Ca^{2+} , Sr^{2+} , Mn^{2+} , Al^{3+} , Ga^{3+} , In^{2+} , La^{3+} , Lu^{3+} , I^{7+} , I^{5+} , CO_2	Fe^{2+} , Co^{2+} , Ni^{2+} , Ca^{2+} , Zn^{2+} , Pb^{2+} , Sn^{2+} , Sb^{3+} , Bi^{3+} , Rh^{3+} , SO^2 , NO^+ , GaH_3	Cu^+ , Ag^+ , Au^+ , Ti^+ , Hg^+ , Pd^{2+} , Cd^+ , Pt^{2+} , Hg^{2+} , I^+ , Br^+ , I_2 , Br_2 Zero valent metal atoms

Soft and Hard Acids: A hard acid, like a hard base, is difficult to polarise. A cationic hard acid, such as Al^{3+} , generally has a small size, high positive charge and has a noble gas electronic configuration.

Soft acids, like soft bases, are readily polarised, have a large size, low positive or zero charge and do not have a noble gas electronic configuration.

Pearson's SHAB principle and stability of the complex $A : B$ (1963)

Consider the typical Lewis acid-base reaction :



Soft and Hard Acids and Bases (SHAB) principle is very helpful in making a prediction of the stability of the complex $A : B$, proposed by Ralph G. Pearson (1963). According to this principle the complex $A : B$ is most stable when A and B are either both soft or both hard. The complex is least stable when one of the reactants is very hard and the other one is very soft.

This principle also means that if there is a choice of reaction between an acid and two bases, or between a base and two acids, a hard acid will prefer to combine with a hard base and a soft acid will prefer to combine with a soft base and thus a more stable product will be obtained.

Applications of the SHAB principle: Let us consider some typical examples

(i) AgI_2^- is stable, but AgF_2^- does not exist

It will be seen From Table that Ag^+ is a soft acid, F^- is a hard base and I^- is a soft base. Hence AgI_2^- (soft acid + soft base) is a stable complex and AgF_2^- (soft acid +hard base) does not exist. Similarly It can also be shown that CoF_6^{3-} (hard acid +hard base) is more stable than CoI_6^{3-} (hard acid-soft base).

(ii) Consider the case of $\text{Hg}(\text{OH})_2$ and HgS . $\text{Hg}(\text{OH})_2$ dissolves readily in acidic aqueous solution but HgS does not. Because HgS (soft acid+soft base) will be more stable than $\text{Hg}(\text{OH})_2$ (soft acid+hard base).

(iii) The existence of certain metal ores can also be rationalized by applying the SHAB principle. Thus, hard acids such as Mg^{2+} , Ca^{2+} , and Al^{3+} occur in nature as MgCO_3 , CaCO_3 , and Al_2O_3 , and not as sulphides (MgS , CaS , and Al_2S_3), since the anions CO_3^{2-} and O^{2-} are hard bases and S^{2-} is a soft base. Soft acids such as Cu^+ , Ag^+ and Hg^{2+} , on the other hand, occur in nature as sulphides. The borderline acids such Ni^{2+} , Cu^{2+} , Pb^{2+} occur in nature both as carbonates and sulphide. The combination of hard acids and hard bases occurs mainly through ionic bonding as in $\text{Mg}(\text{OH})_2$, and that of soft acids and soft bases occurs mainly by covalent bonding as in HgI_2 .

5. THE USANOVICH CONCEPT-THE POSITIVE NEGATIVE SYSTEM :

The most comprehensive of all the acid-base theories is the Usanovich concept according to which an acid is any species capable of giving cations, combining with anions or electrons or neutralising a base to give a salt. In other words an acid is a cation, a cation donor, an electron pair acceptor.

A base is defined as any species capable of giving up anions or electrons, combining with cation or neutralizing an acid to give a salt.

Obviously this concept includes all the previous acid-base definitions. The acidic and basic character of a molecule depends on the valence of the atoms of which the molecule is composed.

The acidic character of the elements increases on moving from left to right in a period in periodic table and basic character increases on passing from top to bottom of a group of the periodic table. Thus the oxide of alkali and alkaline earth metals are essentially basic whereas those of N and S are acidic. The acidic character of a molecule increases with the increase in the oxidation state of the molecule. Specific examples of Usanovich concept :

Examples of acid-base reactions	Explanation
Acid + Base → Salt	
$\text{SO}_3 + \text{Na}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4$	Na_2O gives O^{2-} ion; SO_3 combine with O^{2-} ion: $\text{Na}_2\text{O} \rightarrow 2\text{Na}^+ + \text{O}^{2-}$
	$\text{SO}_3 + \text{O}^{2-} \rightarrow \text{SO}_4^{2-}$
	$2\text{Na}^+ + \text{SO}_4^{2-} \rightarrow \text{Na}_2\text{SO}_4(\text{salt})$
$\text{Fe}(\text{CN})_2 + 4\text{KCN} \rightarrow \text{K}_4[\text{Fe}(\text{CN})_6]$	KCN gives CN^- ion, $\text{Fe}(\text{CN})_2$ combined with CN^- ion.
	$4\text{KCN} \rightarrow 4\text{K}^+ + 4\text{CN}^-$
	$\text{Fe}(\text{CN})_2 + 4\text{CN}^- \rightarrow [\text{Fe}(\text{CN})_6]^{4-}$
	$4\text{K}^+ + [\text{Fe}(\text{CN})_6]^{4-} \rightarrow \text{K}_4[\text{Fe}(\text{CN})_6]$
$2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl}$	Na atoms lose an electron; Cl atoms combine with this electron.
	$2\text{Na} \rightarrow 2\text{Na}^+ + 2\text{e}^-$
	$2\text{Cl} + 2\text{e}^- \rightarrow 2\text{Cl}^-$
	$2\text{Na}^+ + 2\text{Cl}^- \rightarrow 2\text{NaCl}$

Utility : This concept is most general, hence classifying together all examples of acids and bases.

Limitations : (i) It is extremely general.

(ii) It includes many reactions such as oxidation-reduction reactions which can perhaps be better considered from some other point of view.

(iii) This theory considers all chemical reactions as acid-base reactions.

Reference book : Selected topics in inorganic chemistry by :Wahid U.Malik, G.D.Tuli and R.D.Madan

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