

## **Module -V**

### **ACCURACY**

- The accuracy of a determination may be defined as the concordance between it and the true or most probable value.
- The systematic errors cause a constant error (either too high or too low) and thus affect the accuracy of a result.
- For analytical methods there are two possible ways of determining the accuracy; the so-called absolute method and the comparative method.

#### **Absolute method**

- A synthetic sample containing known amounts of the constituents in question is used.
- Known amounts of a constituent can be obtained by weighing out pure elements or compounds of known stoichiometric composition.
- These substances, primary standards, may be available commercially or they may be prepared by the analyst and subjected to rigorous purification by recrystallisation, etc.
- The substances must be of known purity.
- The test of the accuracy of the method under consideration is carried out by taking varying amounts of the constituent and proceeding according to specified instructions.
- The amount of the constituent must be varied, because the determinate errors in the procedure may be a function of the amount used.
- The difference between the mean of an adequate number of results and the amount of the constituent actually present, usually expressed as parts per thousand, is a measure of the accuracy of the method in the absence of foreign substances.
- The constituent in question will usually have to be determined in the presence of other substances, and it will therefore be necessary to know the effect of these upon the determination.
- This will require testing the influence of a large number of elements, each in varying amounts - a major undertaking.
- The scope of such tests may be limited by considering the determination of the component in a specified range of concentration in a material whose composition is more or less fixed both with respect to the elements which may be present and their relative amounts.
- It is desirable, however, to study the effect of as many foreign elements as feasible.
- In practice, it is frequently found that separations will be required before a determination can be made in the presence of varying elements; the accuracy of the method is likely to be largely controlled by the separations involved.

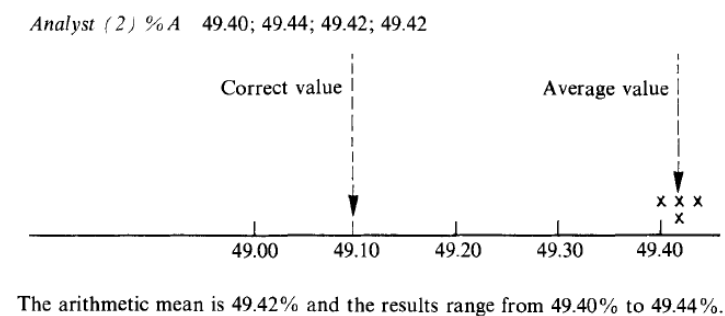
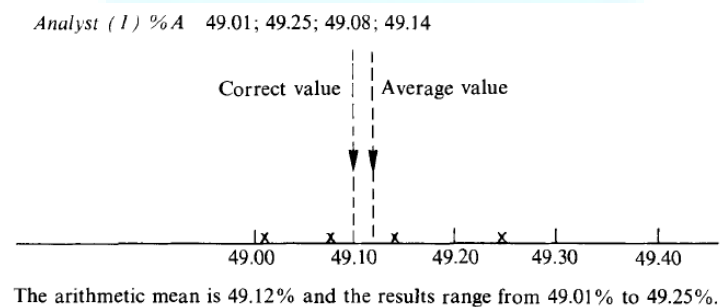
#### **Comparative method**

- Sometimes, as in the analysis of a mineral, it may be impossible to prepare solid synthetic samples of the desired composition.
- It is then necessary to resort to standard samples of the material in question (mineral, ore, alloy, etc.) in which the content of the constituent sought has been determined by one or more supposedly 'accurate' methods of analysis.

- This comparative method, involving secondary standards, is obviously not altogether satisfactory from the theoretical standpoint, but is nevertheless very useful in applied analysis.
- If several fundamentally different methods of analysis for a given constituent are available, e.g. gravimetric, titrimetric, spectrophotometric, or spectrographic, the agreement between at least two methods of essentially different character can usually be accepted as indicating the absence of an appreciable systematic error in either (a systematic error is one which can be evaluated experimentally or theoretically).

## PRECISION

- Precision may be defined as the concordance of a series of measurements of the same quantity. Accuracy expresses the correctness of a measurement, and precision the 'reproducibility' of a measurement.
- Precision always accompanies accuracy, but a high degree of precision does not imply accuracy.
- A substance was known to contain  $49.10 \pm 0.02$  per cent of a constituent A.
- The results obtained by two analysts using the same substance and the same analytical method were as follows.



We can summarise the results of the analyses as follows.

- The values obtained by Analyst 1 are accurate (very close to the correct result), but the precision is inferior to the results given by Analyst 2. The values obtained by Analyst 2 are very precise but are not accurate.
- The results of Analyst 1 face on both sides of the mean value and could be attributed to random errors. It is apparent that there is a constant (systematic) error present in the results of Analyst 2.

- Precision was previously described as the reproducibility of a measurement.

- However, the modern analyst makes a distinction between the terms 'reproducible' and 'repeatable'. On further consideration of the above example:

(c) If Analyst 2 had made the determinations on the same day in rapid succession, then this would be defined as 'repeatable' analysis. However, if the determinations had been made on separate days when laboratory conditions may Vary, this set of results would be defined as 'reproducible'.

Thus, there is a distinction between a within-run precision (repeatability) and a between-run precision (reproducibility).

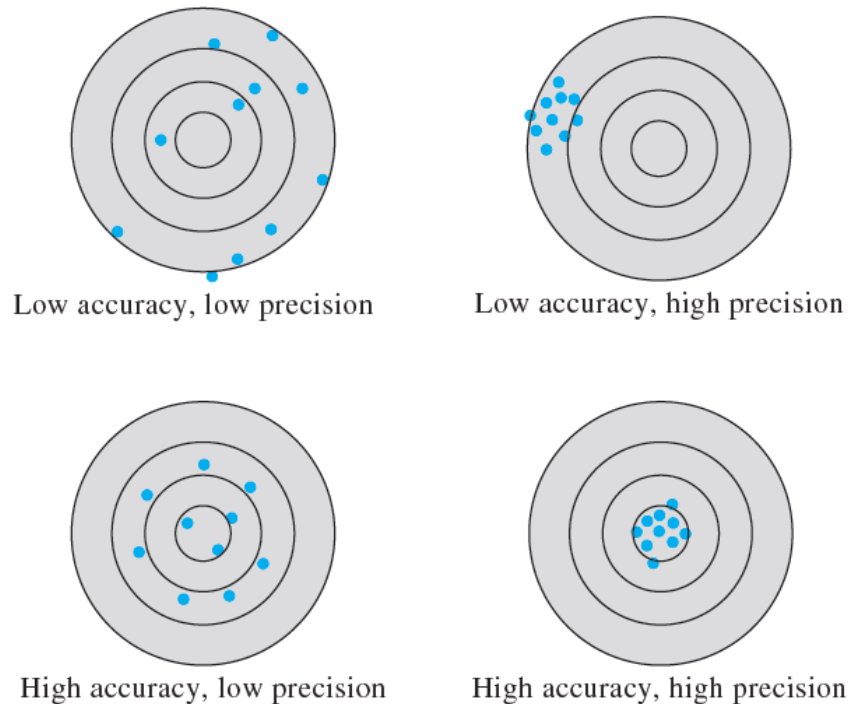


Illustration of accuracy and precision using the pattern of darts on a dartboard

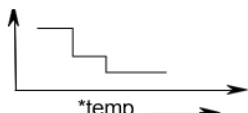
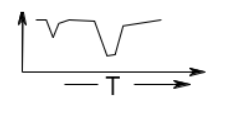
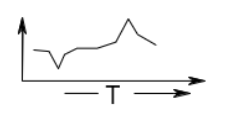
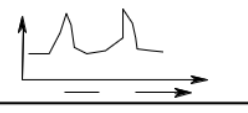
## Thermal methods of analysis

- Techniques in which some physical parameters of the system are determined and recorded as a function of temperature.
- The program may involve heating or cooling at a fixed rate of temperature change, or holding the temperature constant at different time spam. The graphical results obtained are called the thermogram.
- These methods are usually applied to solids, liquids and gels to characterize the materials for quality control.

The advantages of TA over other analytical techniques can be summarized as follows:

- (1) The samples can be studied over a wide temperature range using various temperature programs.
- (2) Almost any physical from of sample (solid, liquid or gel) can be accommodated using a variety of sample vessels.
- (3) A small amount of sample (0.1  $\mu\text{g}$  – 10 mg) is required.
- (4) The atmosphere of the sample can be standardized.
- (5) The time required to complete an experiment range from several minutes to hours.

### Some Thermal Analysis Techniques

TECHNIQUE	ABBREVIATION	PROPERTY	NATURE OF PLOT
Thermogravimetry	TG	Mass	
Derivative thermogravimetry	DTG	$dm/dt$	
Differential Thermal Analysis	DTA	$T_s - T_r (\Delta T)$	
Differential Scanning Calorimetry	DSC	Heat flow, $dH/dt$	
Evolved Gas Analysis	EGA	Gases evolved	

## **Thermogravimetric Analysis (TGA)**

Thermogravimetric analysis is the study of the changes in weight of a sample as a function of temperature. The technique is useful strictly for transformations involving the absorption or evolution of gases from a specimen.

Suitable samples for TGA are solids that undergo one of the two general reactions:



## Structure & Bonding

### LOCALIZED CHEMICAL BONDING

*Localized chemical bonding* may be defined as bonding in which the electrons are shared by two and only two nuclei.

#### Covalent Bonding

According to G.N. Lewis, A covalent bond is formed by sharing of electrons, each atom contributing one or more electrons to form the shared pair or pairs. In this way, each of the bonded atoms attains the stable electronic configuration of the nearest noble gas. The two bonded atoms are held together by shared pair or pairs of electrons. The covalent bond formed by sharing of one electron pair is called a single bond (as in hydrogen and chlorine molecules), whereas that formed by sharing of two electron pairs (as in oxygen molecule) and three electron pairs (as in nitrogen molecule) are called double and triple bonds, respectively. Double and triple bonds are collectively called multiple bonds.

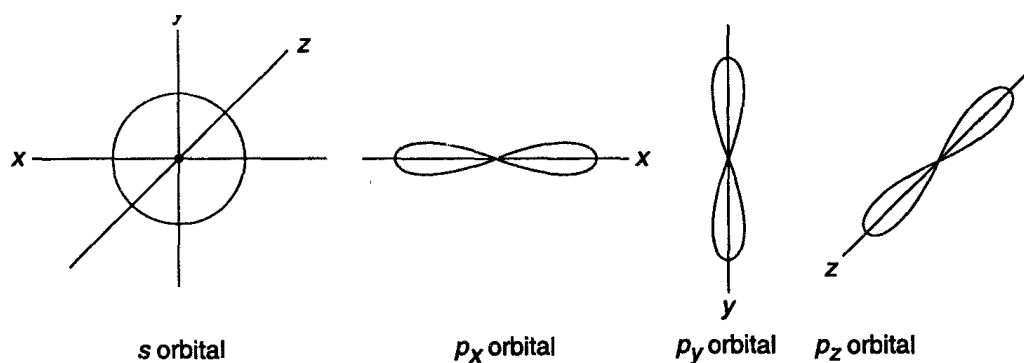
The structures in which the shared electron pair(s) as well as all the unshared valency electrons (non-bonding electrons) of bonded atoms are shown by dots were first used by Lewis and they are known as Lewis structures. In Lewis structures, the symbol of the atom represents kernel (nucleus + electrons except valency electrons) but not only nucleus. The electrons of the outermost shell of an atom are called valency (valence) electrons.

#### Atomic Orbitals

An atomic orbital is defined as the definite region in three-dimensional space around a nucleus where there is high probability of finding an electron of specific energy. In organic chemistry, we are mainly concerned with *s* and *p*-orbitals, hence the shapes and orientations of these orbitals are described below:

An *s* orbital has spherical shape. The atomic nucleus is in the centre of *s* orbital and the orbital is spherically symmetrical about the nucleus.

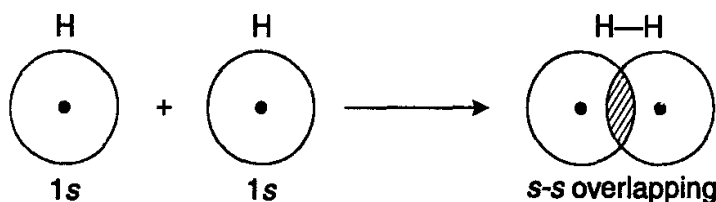
A *p* atomic orbital consists of two equal lobes forming a dumb-bell shape. The two lobes do not touch each other at the nucleus, thus the probability of finding electrons in this region is zero and it is called the nodal plane. There are three *p* orbitals of equal energy. They are directed perpendicular to each other just as Cartesian co-ordinates and are designated as  $P_x$ ,  $P_y$  and  $P_z$  corresponding to their axes of orientation.



**Fig. 1.1. Shapes of *s* and *p* orbitals.**

## Valence Bond Theory

The valence bond (VB) theory of bonding is mainly based on the work of Heitler, London, Pauling and Slater. According to this theory, a covalent bond is formed by overlapping of two half-filled atomic orbitals containing electrons of opposite spins. For example, let us consider the formation of a hydrogen molecule ( $H_2$ ) from two hydrogen atoms. When two hydrogen atoms come enough close to each other, a covalent bond is formed between them by overlapping of their half-filled  $1s$  orbitals containing electrons of opposite spins. The greater the overlapping, the stronger is the resulting bond. However, total overlapping is prevented by repulsion between the nuclei.



### 2. Formation of H—H covalent bond according to the valence bond theory.

The principles of overlap can be summarized as :

- Only those orbitals overlap which participate in the bond formation. Orbitals of the bonded atoms retain their individual identity.
- The greater overlapping of the atomic orbitals leads to a lowering of energy due to the attractive forces between electrons and the nuclei between atomic orbitals. Thus the greater the overlap between atomic orbitals, the stronger is the covalent bond (This is known as principle of maximum overlap).
- The direction of the electron density in the bonds determines the bond angle.

#### Limitations of Valence Bond Theory:

The following are chief drawbacks of VB theory :

- It has to introduce hypothetical concepts of hybridization, resonance and hyperconjugation

to explain the formation and structures of various molecules.

- It does not explain why atomic orbitals of bonded atoms should retain their identity, whereas

the nuclei of approaching atoms are bound to affect nearly all atomic orbitals of each other.

- It does not explain the paramagnetic behavior of oxygen molecule.

#### Molecular Orbital Theory

The molecular orbital (MO) theory of bonding is mainly based on the work of Hund, Lennard-Jones, Huckle and Mullikan. According to this theory the molecule is regarded as being formed by the overlap of all atomic orbitals ( $n$ ) of the bonded atoms. When two atoms are brought closer to one another, their all atomic orbitals combine to give a set of new molecular orbitals (wave functions) in equivalent number ( $n$ ) that encompass the entire molecule. Thus, every molecule is supposed to have orbitals associated with it in much the same way as a single isolated atom has. The Pauli's exclusion principle is applied to the MO's in the same way as it is applied to the atomic orbitals. MO's also follow Aufbau principle and Hund's rule. According to molecular orbital theory, the atomic orbitals combine (overlap) and form a resultant

orbital known as the molecular orbital in which the identity of both atomic orbitals is lost. All the electrons pertaining to, both the atoms are considered to be moving along the entire molecule under the influence of all the nuclei.

### Basic Principles of Molecular Orbital Theory

- (1) When nuclei of two atoms come close to each other, their atomic orbitals interact resulting in the formation of molecular orbitals (MO). In molecule atomic orbitals of atoms lose their identity after the formation of molecular orbitals.
- (2) Each molecular orbital may be described by the wave function  $\psi$  which is known as MO, wave function,  $\psi$  represents the electron density.
- (3) Each MO wave function  $\psi$  is associated with a set of quantum numbers which represent energy and shape of the occupied MO.
- (4) Each MO wave function  $\psi$  is associated with a definite energy value. The total energy of the molecule is the sum of the energies of the occupied MO.
- (5) Molecular orbitals follow Pauli's exclusion principle, Hund's rule and Aufbau principle.
- (6) Each electron in a molecular orbital belongs to all the nuclei present in the molecule.
- (7) Each electron moving in the molecular orbital is having clockwise or counter-clockwise
- (8) Number of molecular orbitals are always equal to the number of atomic orbitals.

The molecular orbitals can be obtained by the method of Linear combination of atomic orbitals (LCAO). Let two atoms A and B form AB molecule which is hetero diatomic molecule. Their atomic orbitals are represented by  $\psi_A$  and  $\psi_B$  respectively. There are following two ways of their combination:

- (i) **Additive Overlap:** Additive overlap is also known as positive overlap or ++ overlap. In this type of linear combination the  $\psi_B$  positive lobe (*i.e.*, the lobe having positive sign) of  $\psi_A$  overlaps with the positive lobe of, thus a molecular orbital is formed. This molecular orbital has lower energy than that of atomic orbitals of atom A and B due to attraction between the nuclei of A and B. Such type of molecular orbitals are known as bonding molecular orbitals (BMO) and represented as " $\sigma$ "
- (ii) **Subtractive Overlap:** Subtractive overlap is also known as negative overlap or -overlap. In this type of the linear combination the positive lobe of  $\psi_A$  overlaps with the negative lobe of  $\psi_B$ , thus a molecular orbital is formed. This molecular orbital has higher energy than that of atomic orbitals of atom A and B due to repulsion between nuclei of A and B. Such type of molecular orbitals are known as anti-bonding molecular orbitals (ABMO).



## Combination of Atomic Orbitals to Form Molecular Orbitals

### (i) Combination of $s$ -orbitals :

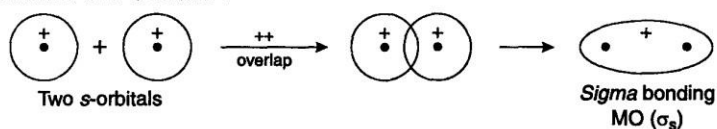


Fig. 1.4.

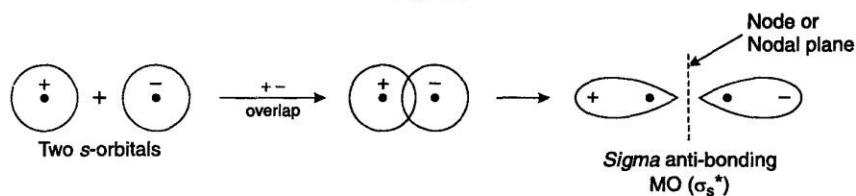
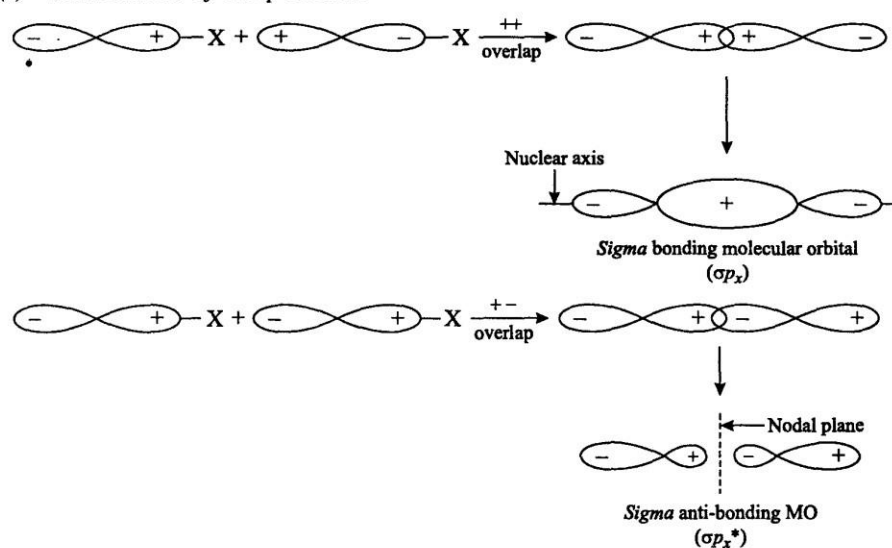


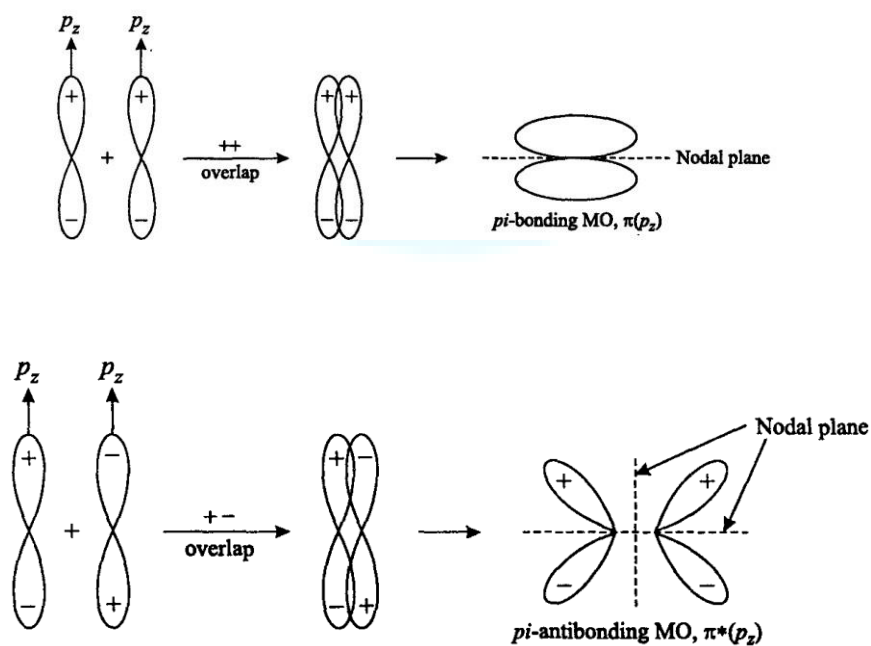
Fig. 1.5.

### Combination of $p$ -orbitals :

#### (i) Combination of two $p$ -orbitals



#### (ii) Combination of two $p_z$ -atomic orbitals



## Comparison between VB and MO theories

### (A) Similarities between VB and MO theories:

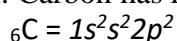
- They account for the directional nature of the bond.
- Bond results by the overlapping of two orbitals of minimum energy.
- Electronic charge persists in between two atomic nuclei in bond formation.
- Atomic orbitals should be of same energy, should overlap and should have same symmetry.

### (B) Dissimilarities between VB and MO theories :

VB Theory	MO Theory
Inter-atomic orbitals are produced by multiplying, two unpaired electrons.	Molecular orbitals are formed by LCAO of all exchanging and combination of wave functions of atomic orbitals from the valency shell of two
Orbitals of the bonded atoms retain their individual identity.	Orbitals of bonded atoms lose their individual identity.
Orbitals are monocentric	Molecular orbitals are polycentric

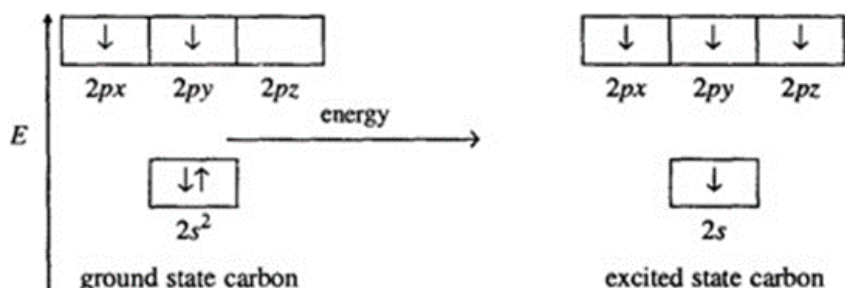
## Hybridization

The chemical properties of an element depend on the electronic configuration of the outermost shell. Carbon has four electrons in its outermost shell.



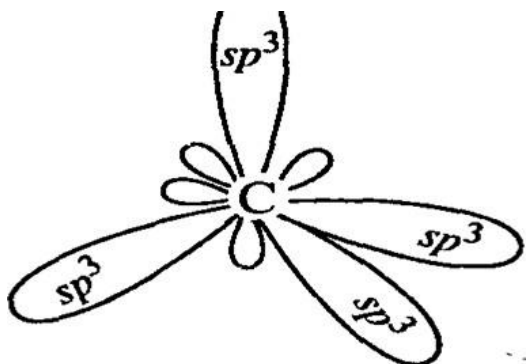
The valency of an element is usually defined as the number of half-filled orbitals present in the outermost shell of its atom. Thus, according to the ground state electronic configuration of carbon, it should be divalent, but actually it is tetra covalent in most of its compounds.

Carbon's tetravalency is explained by promoting one,  $2s$ , electron to a  $2p_z$  orbital. Some energy must be supplied to the system in order to effect this promotion. This promotion requires energy about 96 kcal/mole, but this energy is more than regained by the concurrent formation of chemical bonds.



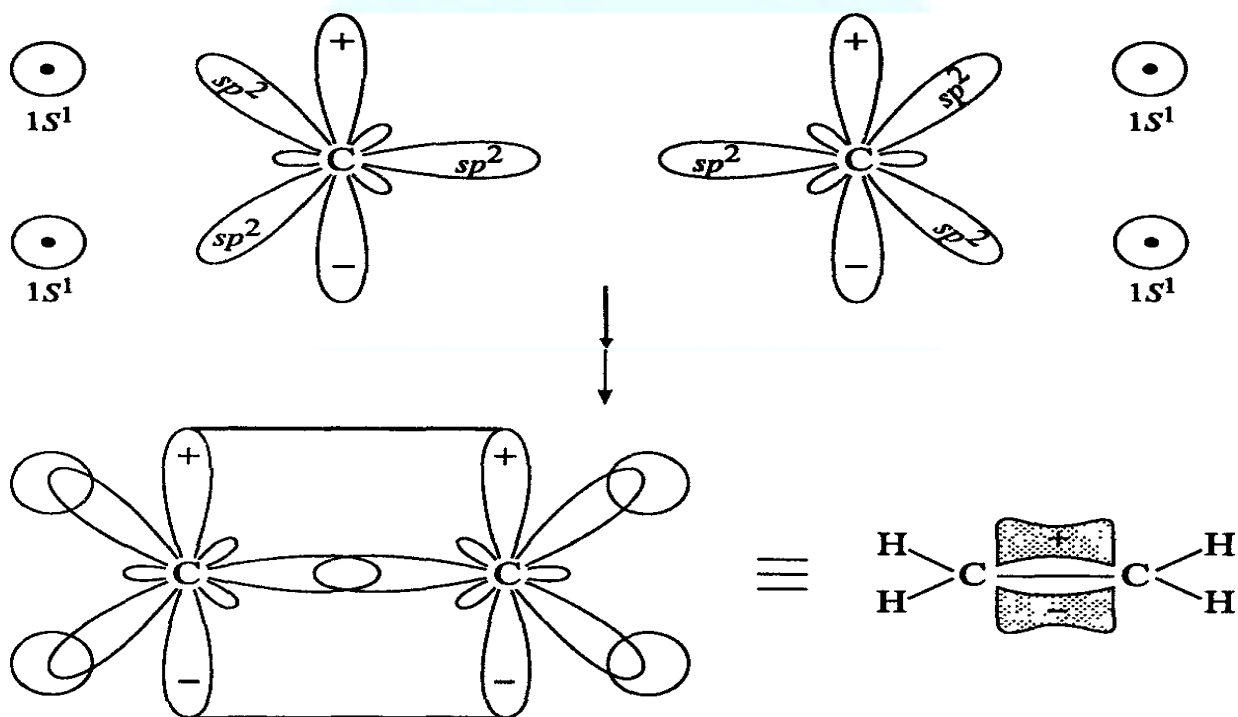
**Promotion of an electron in carbon allowing formation of four covalent bonds**

The promotion of an electron from 2s orbital to one of the vacant 2p orbitals explains the observed valencies of this element. But there is one difficulty that three of the electrons have *p-orbitals* and the fourth one has s-orbital, the bond angle is equal to  $109.5^\circ$  in methane and all four bonds are equivalent.



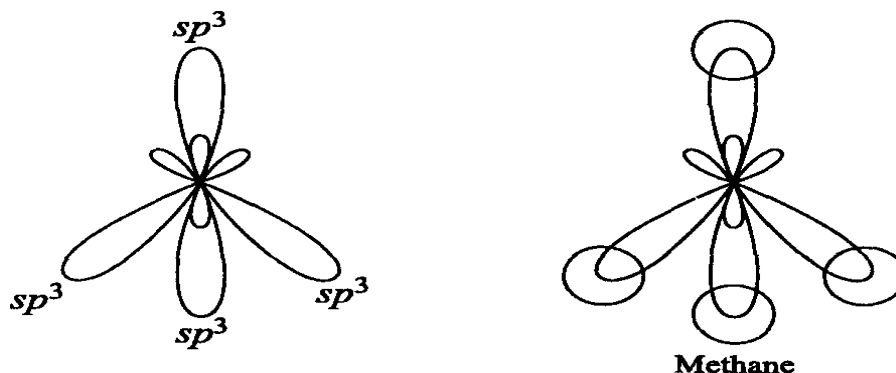
**(2)  $sp^2$  or Trigonal Hybridization :**

In this type of hybridization one sand 2p orbitals of the valence shell of central atom of the given molecule combine to form three  $sp^2$ -hybrid orbitals as shown below:



### (3) $sp^3$ or Tetrahedral Hybridization:

In this hybridization one  $s$  and three  $p$ -orbitals of the valence shell of central atom of the given molecule combine to form four  $sp^3$  hybrid orbitals.



### DELOCALIZED CHEMICAL BONDING

*Delocalized chemical bonding* may be termed as bonding in which the electrons are shared by more than two nuclei. Molecules having conjugated systems exhibit delocalization of electrons, *i.e.*, they have delocalized bonds. For example, resonance, hyperconjugation and aromaticity involve delocalized chemical bonding.

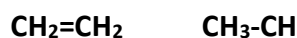
#### Resonance

A concept that makes valence bond theory useful for the structural description of complex molecules is resonance theory. Resonance theory is an extension of valence bond theory which recognizes that more than one Lewis structure can be written for many molecules. Resonance is hypothetical state of a chemical species in which its electronic structure can be hypothetically represented by two or more resonating structures, each differing only in the distribution of electrons but not of the constituent atoms. The properties of the species will not be those to be expected of any of the resonating structures, but they will be those to be expected from a combination (or hybridization) called a resonance hybrid of them. The resonance hybrid is the real structure of the chemical species.

Thus the chemical species has a single structure (*i.e.*, resonance hybrid) of its own by the conventional Lewis method. So we take the help of other possible though non-existent, structures (*i.e.*, canonical structures) which could be represented by Lewis method. Generally, the resonance hybrid is projected on the paper by writing down all the resonating structures and placing a double-headed arrow between each pair. Its usefulness in organic chemistry lies in its being a convenient way of depicting electron delocalization. Resonance theory is particularly useful in describing conjugated species. Arguments based on resonance theory are usually made in a qualitative way.

The elements of resonance theory that are necessary for qualitative applications are as follows:

- (1) All the canonical structures must be written according to the Lewis method showing bonds, lonepair of electrons and formal charges where required.
- (2) The positions of the atomic nuclei of the chemical species must remain unchanged in all the resonating structures. Thus (1) and (2) are not canonical structures.



1

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- (3) To each resonating structures, only the  $\pi$ -bonds can be converted to a lone-pair of electrons and *vice-versa*. Thus the resonance hybrid of alkenes may be written as :



## Resonance Energy or Delocalization Energy

The resonance hybrid of a species is a more stable structure than anyone of the resonating structures contributing to it. The resonance energy is a measure of the extra stability of the resonance hybrid. It is defined as the difference in energy between the actual structure of the species and the most stable of the hypothetical structures (*i.e.*, canonical structures). The resonance energy of a molecule may be calculated by anyone of the following methods :

(i) Resonance energy = (Observed heat of formation) - (Calculated heat of formation of the stablest

resonating structure)

(ii) Resonance energy = (Observed heat of combustion)- (Calculated heat of combustion of the stablest

resonating structure)

(iii) Resonance energy = (Observed heat of hydrogenation) - (Calculated heat of hydrogenation of the stablest

resonating structure)

## Hyperconjugation

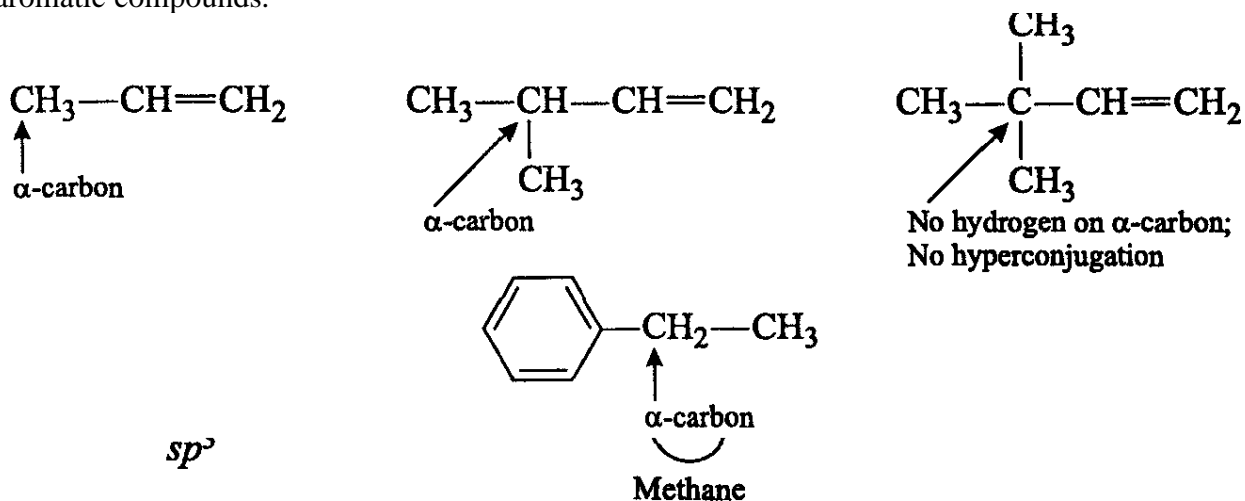
Chemical and structural evidence indicate that alkyl substituents (having hydrogen on *alpha* carbon) on a carbon-carbon double bond act as electron donors to the *pi* system. The delocalization of  $\sigma$ -electrons through conjugation with  $\pi$ -electrons (or with vacant or half-filled *p* orbital) is known as hyperconjugation (or Baker-Nathan effect or no-bond resonance). The hyperconjugative effect was first of all observed by Baker and Nathan (1935).

Structural requirement of hyperconjugation : Any organic species can show hyperconjugation phenomenon if it will fulfill the following conditions:

(1) Compound should have at least one  $sp^2$  hybrid carbon of alkanes, arene carbocation or free radical

(2) *Alpha* carbon with respect to  $sp^2$  hybrid carbon should have at least one hydrogen Thus hyperconjugation is of three types :

(1)  $\sigma$  (C-H),  $\pi$ : conjugation: This type of conjugation occurs in alkenes and alkyl substituted aromatic compounds.



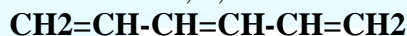
### Aromaticity. The Huckle ( $4n + 2$ ) $\pi$ Rule

It is clear that benzene is an especially stable molecule. A number of these compounds have a similar special stability, which is called *aromaticity*. To be aromatic a compound must conform to all the following criteria :

- (1) The molecule should be cyclic.
- (2) There should be a p-orbital on every atom of an aromatic ring, *i.e.*, cyclic molecule is fully conjugated.
- (3) Aromatic rings are planar. This planarity allows the p-orbitals on every atom to overlap.
- (4) The cyclic arrangement of p-orbitals in an aromatic compound must contain  $(4n + 2)\pi$  - electrons, where  $n$  is an integer (0, 1, 2, 3 ... ). In other words, aromatic compounds have 2, 6, 10, 14, 18, ... ,  $\pi$  electrons.

These criteria for aromatic behavior were first recognized in 1931 by Erich Huckel. They are often called collectively the Huckle  $4n + 2 \pi$  rule or simply the  $4n + 2 \pi$  rule. This rule is mainly used for annulenes. Annulene is a general name for monocyclic hydrocarbons with alternating single and double bonds. The ring size of an annulene is indicated by a number in bracket. Since the carbon atoms occur as doubly bonded pairs, an annulene must have an even number of carbons. Thus benzene is [6] annulene, cyclooctatetraene is [8] annulene. The general formula of annulenes is  $(CH)_{2n}$ .

Benzene conforms to the  $(4n + 2) \pi$  rule because it contains a planar, continuous ring of atoms with a total of six  $\pi$  -electrons. The alkenes 1, 3, 5-hexatriene is not aromatic.



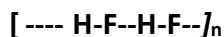
**1, 3, 5-hexatriene**

This compound has six 1t-electrons and all p-orbitals are parallel. However, this compound is not aromatic because the six 1t-electrons are not present in a *cyclic* arrangement, this compound does not meet the criteria of aromaticity.

### Hydrogen Bonding

When a hydrogen atom is bonded covalently to a highly electronegative atom having a small nucleus (like O, N, F, S, etc.), the bonding electron pair is drawn almost completely towards the electronegative atom. Such hydrogen atom acquires a special ability to attract and associate with the other electron rich atoms or group of atoms (O, N, F, etc.) towards itself. This attraction or weak link established between hydrogen and a second electronegative atom or group is known as hydrogen bond. In hydrogen bonding hydrogen atom may act as a bridge between two electronegative atoms (same or different), holding one electronegative atom by a covalent bond and the other by electrostatic force. This kind of electrostatic attraction is a special case of dipole-dipole association and is of great

practical importance. Usually a hydrogen bond is represented by a dashed line rather than by the solid line used for a covalent bond.



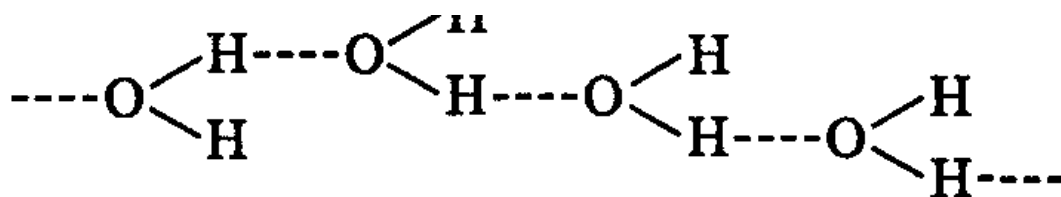
**Covalent bond**

**Hydrogen bond**

**The hydrogen bonds are of two types :**

#### a. Intermolecular hydrogen bond:

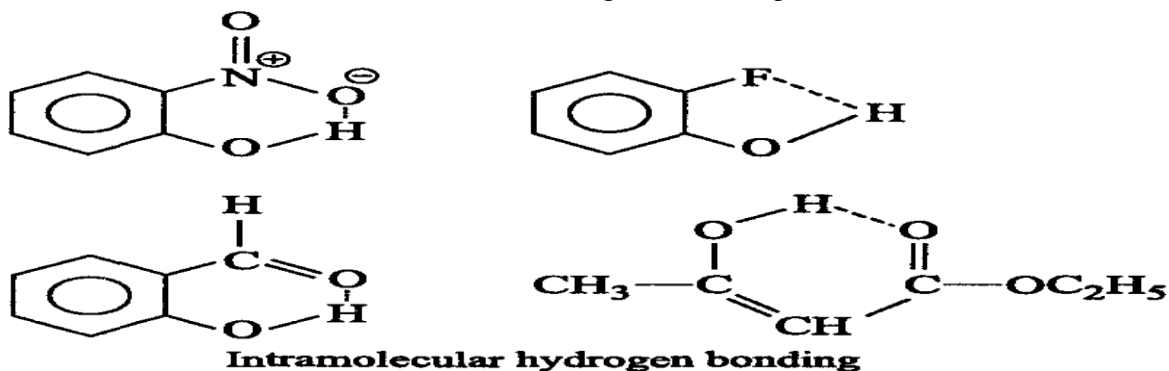
Intermolecular hydrogen bond is formed between atoms of two or more molecules, resulting in the association of molecules. For example, water and alcohols are associated as polymeric aggregates in liquid and solid states whereas carboxylic acids and amides exist as dimer in the liquid and gaseous phase due to intermolecular hydrogen bonding.



**Polymeric form of water molecule (intermolecular hydrogen bond)**

**b. Intramolecular hydrogen bonding:**

Intramolecular hydrogen bond is formed between two atoms within the same molecule. This results in the formation of five or six membered ring (chelate ring).





## Chemical Periodicity

The first elements that were discovered were shiny metals that melted out of rocks heated in fires. The first elements discovered were copper, silver and gold. This occurred approximately eight thousand years ago. Lead, tin, iron, mercury, carbon and sulfur were discovered next.

As people began working with metals, the Alchemists searched for a method of turning lead (or other ordinary metals) into gold. They were not successful, but they did discover other elements in the process. Scientists began to predict the existence of other elements. Experimentation continued and improved. By 1940 all 90 naturally occurring elements had been discovered. Since then work in nuclear science has led to the discovery of radioactive elements.

Only about one quarter of the elements occur in the free (or elemental) state. The others are found in compounds - two or more elements chemically bonded together.

**Metals** - More than three quarters of the known elements are metals. Metals share similar properties:

- good conductors of heat and electricity
- luster
- malleable and ductile
- high densities
- high boiling points and melting points
- resist stretching and twisting
- solids at room temperature

**Nonmetals** - no luster

- poor conductors
- may be solid, liquid or gas
- low densities
- low melting and boiling points

**Metalloids (or Semimetals)** - have properties of both metals and nonmetals

### The Development of the Periodic Table

As more elements were discovered, some patterns of similarities in elements were recognized. Scientists began trying to organize the elements. Dmitri Mendeleev organized the elements in a table. He placed the elements in order of increasing atomic mass. He used columns of different lengths so that elements with similar properties were side by side. He left blank spaces where no known element seemed to fit. He predicted that these blank spaces represented elements which had not been discovered yet. Based on the location of the blanks, he predicted the properties of undiscovered elements. When these elements were discovered, their actual properties were very close to Mendeleev's predictions.

There were a few discrepancies with Mendeleev's table. When the elements were arranged according to increasing atomic mass, some of the elements were out of order. Mendeleev assumed that their masses were not calculated accurately enough. He believed that when more accurate methods were available, that these discrepancies would disappear.

**The Modern Periodic Table:** With the discovery of atomic number (the number of protons in the nucleus) the periodic table was rearranged. The elements are now arranged in order of increasing atomic number. This corrected the discrepancies in Mendeleev's table.

**The Modern Periodic Law** - When the elements are arranged in order of increasing atomic number, there is a periodic repetition of their physical and chemical properties.



## Organization of the Periodic Table

**Periods:-** horizontal rows

properties change from left to right

**Groups (or Families):** - vertical columns

- share similar properties

### Group 1: Alkali Metals

- low densities and melting points
- good electrical conductivity
- the most reactive metals
- react with oxygen and moisture in the air
- they will react violently with water and are stored under oil or kerosene
- due to their reactivity, they are not found uncombined in nature

### Group 2: Alkaline Earth Metals

- similar to the alkali metals, but less reactive, not required to store under oil
- harder than the alkali metals

### Group 17: Halogens

- nonmetals
- do not exist in nature in the uncombined state, but their compounds are common
- form salts with group 1 or 2 metals

### Group 18: Noble Gases

- gases at room temperature
- occur in the atmosphere in very small amounts
- extremely unreactive

### Representative or Main Group Elements

- groups 1,2 and 13 - 18

### Transition Metals: Groups 3 - 12

- typical metals - shiny, and good conductors

**Inner Transition Metals: Lanthanides:** elements 57 - 70

**Actinides:** elements 89 - 102

- typical metals

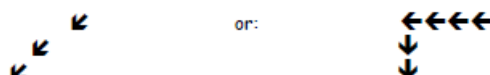
## Trends in the Periodic Table

**Atomic Size:** The size of an atom is generally given in terms of the atomic radius of the atom.

**Group Trends:** Atomic size generally increases as we move down a group of the periodic table. As we descend, electrons are added to successively higher energy levels. The nuclear charge also increases because of additional protons. However, the full nuclear charge is shielded from the outer electrons because of the inner electrons and their distance from the nucleus.

**Period Trends:** Atomic size generally decreases as we move from left to right across a period. As we move across a period, electrons are added to the same energy level. Protons are also added to the nucleus. The effect of the increasing nuclear charge on the outermost electrons is to pull them closer to the nucleus. Atomic size therefore decreases.

In general:



**Ionization Energy** - the amount of energy required to remove an electron from an atom. When the outermost electron is located close to the nucleus, there is a greater attraction between the positive protons (in the nucleus) and the negative electrons. Because of this, more energy is required to remove an electron. When the outermost electrons are located further from the nucleus, the attractive force is less, and it is easier to remove an electron. Therefore, the smaller the atom, the higher

the ionization energy. Group Trends: Ionization energy decreases as we go down a group.

Period Trends: Ionization energy increases as we go across a period.

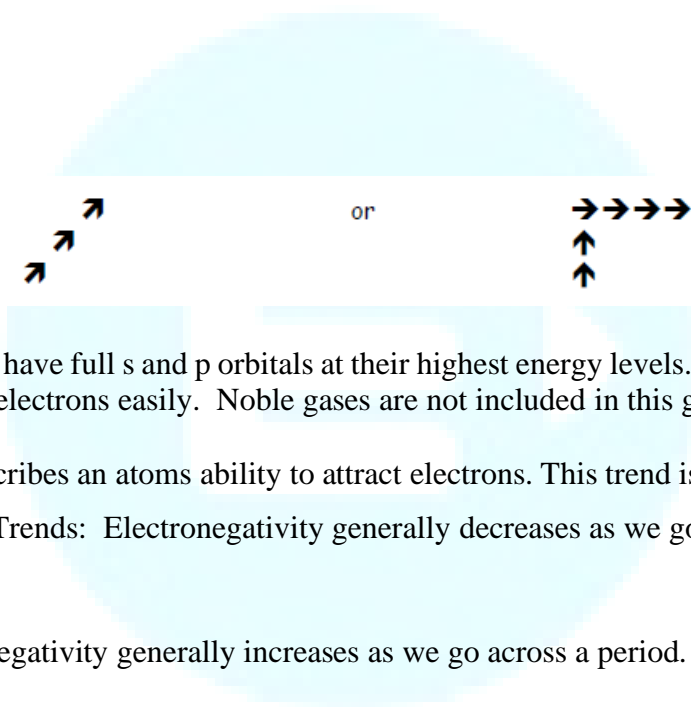
In general:

**Electron Affinity:** The amount of energy released when an electron is added to an atom. When electrons are added close to the nucleus, there is a greater attraction between the negative electron and the positive nucleus and electron affinity is higher. Therefore, the smaller the atom, the higher the electron affinity.

Group Trends: Electronegativity generally decreases as we go down a group.

Period Trends: Electron affinity generally increases as we go across a period.

In general:

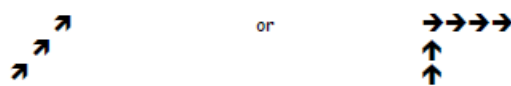


Exceptions: Noble gases have full s and p orbitals at their highest energy levels. Because of this stability, they do not gain or lose electrons easily. Noble gases are not included in this general trend.

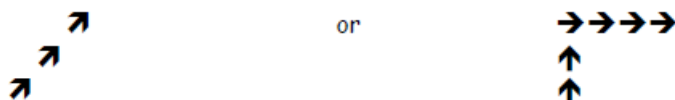
**Electronegativity:** Describes an atoms ability to attract electrons. This trend is similar to electron affinity. Group Trends: Electronegativity generally decreases as we go down a group.

Period Trends: Electronegativity generally increases as we go across a period.

In general:



Exceptions: Noble gases are not included in this general trend.



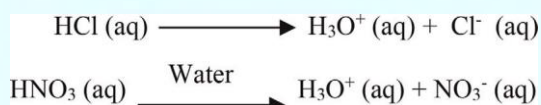
## Theories of acids and bases

### The Arrhenius acid-base theory (the water-ion system)

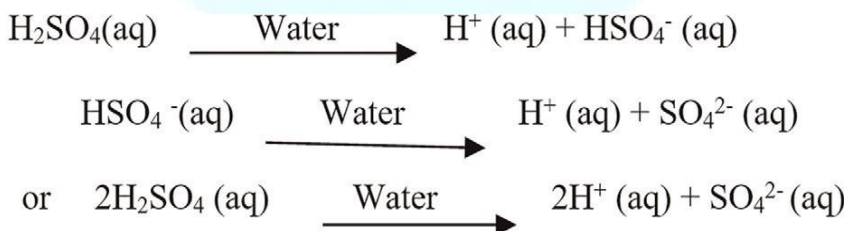
The Arrhenius acid-base theory was proposed by Swedish Svante Arrhenius. It was the first modern approach to acid-base concept. This theory is quite simple and useful. According to Arrhenius theory, acids are the compound that increases the concentration of  $\text{H}^+$  or proton in aqueous solution. The released  $\text{H}^+$  ion or proton is not free-floating proton, it exists in combined state with the water molecule and forms hydronium ion ( $\text{H}_3\text{O}^+$ ). The common examples of Arrhenius acid includes  $\text{HCl}$  (hydrochloric acid),  $\text{H}_2\text{SO}_4$  (sulphuric acid),  $\text{HNO}_3$  (nitric acid), etc.



When it is dissolved in water, then:



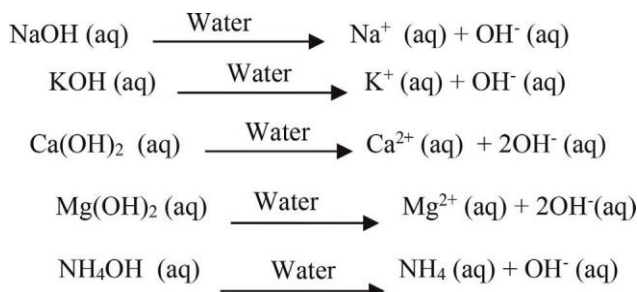
The acids like  $\text{HNO}_3$ ,  $\text{HCl}$ , etc. gives one proton on dissociation, called monoprotic acids. The acids like  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , etc. which having more than one hydrogen atoms and gives more than 1  $\text{H}^+$  ions on dissociation, called polyprotic acids. It is not necessary that polyprotic acids are stronger than monoprotic acids.



Similarly, Arrhenius bases are compounds that increase the concentration of  $\text{OH}^-$  or hydroxide ion in aqueous solution or having at least one  $\text{OH}^-$  ion in formula.

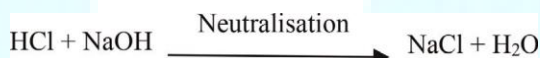
The common examples of Arrhenius base includes  $\text{NaOH}$  (sodium hydroxide),  $\text{KOH}$  (potassium hydroxide),  $\text{Ca(OH)}_2$  (calcium hydroxide),  $\text{Mg(OH)}_2$  (magnesium hydroxide),  $\text{NH}_4\text{OH}$  (ammonium hydroxide), etc.

When sodium hydroxide dissolved in water, it fully dissociates into ions  $\text{Na}^+$  and  $\text{OH}^-$ , this dissociation increases the concentration of hydroxide ions in the solution.

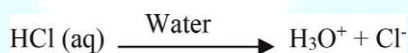


### Neutralization reaction

When Arrhenius acid and Arrhenius base reacts, salt and water is formed as product, the reaction is known as neutralization reaction. For example:

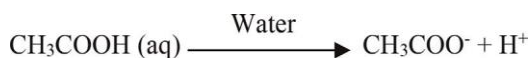


The acids which are completely ionized in aqueous solution, is termed as strong acids such as  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , etc.



Hydrochloric acid is a strong acid. When it dissociates into water, hydronium ion and chloride ions are formed as product. Chloride ions are weak base, but its basicity does not make the solution basic because acidity is overpowering the basicity of chloride ions. The  $\text{H}^+$  ions combine with water molecule and form hydronium ion. In case of strong acid, the concentration of hydronium ion formed is equal to the concentration of the acid whereas in case of weak acids, the concentration of hydronium ions in solution is always less than the concentration of hydrogen ions.

Whereas the acids which are weakly ionized in aqueous solution, is termed as weak acids such as acetic acid ( $\text{CH}_3\text{COOH}$ ).



In case of weak acids, the concentration of hydronium ion is always

less than the concentration of acid.

Similarly, bases which are completely ionized in aqueous solution, are termed as strong bases such as NaOH, KOH, etc. whereas the bases which are weakly ionized in aqueous solution, is known as weak bases such as ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), etc.

### 1. Utility of Arrhenius concept

This theory explains many phenomena like strength of acids and bases, salt hydrolysis and neutralization.

### 2. Hydrogen ion ( $\text{H}^+$ ) or hydronium ion ( $\text{H}_3\text{O}^+$ )

When electron is removing from hydrogen atom, hydrogen ion  $\text{H}^+$  is formed which is very reactive. But this  $\text{H}^+$  ion does not exist in aqueous solution. Since in aqueous medium, it reacts with water molecule and forms hydronium ion ( $\text{H}_3\text{O}^+$ ). Water is a polar molecule; it has the ability to attract the hydrogen ion ( $\text{H}^+$ ).

The water contains hydrogen and oxygen in which oxygen ( $\text{EN} = 3.5$ ) is more electronegative that pulls the electron density towards it and causing the partial negative charge on the molecule. Due to partial negative charge, it has ability to attract the positively charged hydrogen ion ( $\text{H}^+$ ) and form hydronium ion ( $\text{H}_3\text{O}^+$ ). Hydronium ions are more stable than hydrogen ions.



The hydronium ion is very important factor in chemical reaction that occurs in aqueous solutions [3]. It is formed by the protonation of water.

### 3. Concept of pH

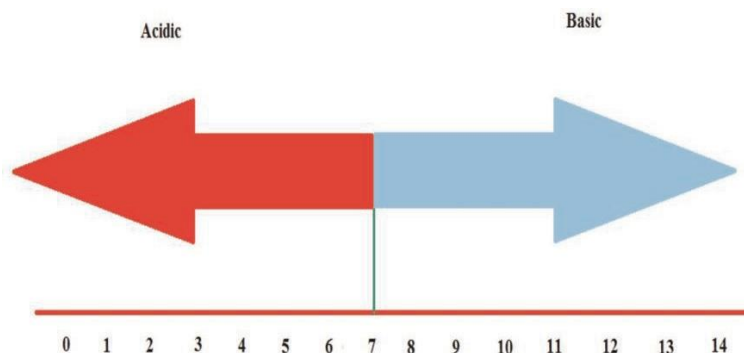
The pH of solution can be determined by the concentration of

$$\text{hydronium ion. } \text{pH} = -\log (\text{H}_3\text{O}^+)$$

From this equation, we can find the pH of pure water. The pH of pure water comes to be 7 that is considered to be neutral. The solution is either acidic or basic depending on the change in the concentration of hydronium ion.

- If the concentration of the hydronium ion in the solution increases means more than  $10^{-7}$  mol/l, pH increases that makes the solution more acidic.





*pH scale.*

- If the concentration of the hydronium ion in the solution decreases means

$<10^{-7}$  mol/l, pH decreases that makes the solution more basic.

#### 4. Amphoteric nature of water

The word amphoteric is derived from Greek word “amphi” that means both (acid and base). Amphoteric substances are those that has potential to act either as an acid or base. For example:  $\text{H}_2\text{O}$  (water) [3].

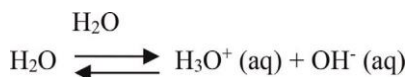


On dissociation, it ionizes into  $\text{H}^+$  and  $\text{OH}^-$  (hydroxide) ion. The presence of  $\text{H}^+$  indicates an acid and the presence of  $\text{OH}^-$  ion indicates a base. Since, water is a neutral molecule. So, it dissociates equally into  $\text{H}^+$  and  $\text{OH}^-$  ion.

According to Arrhenius acid-base theory:

The amphoteric nature of water is very important because most of the acid-base chemical reactions take place in the presence of water. Water is an important amphoteric compound that can act as both an Arrhenius acid or Arrhenius base.

Auto-ionization of water [4];



The  $\text{H}^+$  ion (a bare proton) does not exist in the solution, it forms hydronium ions by hydrogen bonding with the nearest water molecule. Many books refer to the “concentration of hydrogen ions” which is not correct. Because there are no  $\text{H}^+$  ions, only hydronium ions in the solution. Technically, the number of hydronium ions formed is equal to the number of hydrogen ions. So, both can be used.

## 5. Advantages of Arrhenius theory

This theory is used to explain:

- Strength of acid and bases

The strength of Arrhenius acid and Arrhenius base can be determined by the extent to which it dissociates to give  $H^+$  ion or hydroxide ion.

- The properties of acids and bases in aqueous medium.
- Neutralization of acid by reaction with base

## 6. Limitation of Arrhenius acid-base theory

1. This theory is very limited, out of three theories. According to this theory, the solution medium should be aqueous and acid should produce hydrogen ion ( $H^+$ ) or base should produce hydroxide ion ( $OH^-$ ) on dissociation with water. Hence, the substance is regarded as Arrhenius acid or Arrhenius base when it is dissolved in water. For example,  $HNO_3$  is regarded as Arrhenius acid when it is

dissolved in aqueous solution. But when it is dissolved in any other solvent like benzene, no dissociation occurs. This is against the Arrhenius theory.

2. Arrhenius theory is not applicable on the non-aqueous or gaseous reactions because it explained the acid-base behavior in terms of aqueous solutions.
3. In Arrhenius theory, salts are produced in the product which are neither acidic nor basic. So, this theory cannot explain the neutralization reaction without the presence of ions. For example, when acetic acid (weak acid) and sodium hydroxide (strong base) reacts, then the resulting solution is basic. But this concept is not explained by Arrhenius.
4. Arrhenius theory is only applicable to those compounds which having formula  $HA$  or  $BOH$  for acids and bases. There are some acids like  $AlCl_3$ ,  $CuSO_4$ ,  $CO_2$ ,  $SO_2$  which cannot be represented by  $HA$  formula, this theory is unable to explain their acidic behavior. Similarly, there are some bases like  $Na_2CO_3$ ,  $NH_3$ , etc.



which do not represented by BOH formula, this theory is unable to explain their basic behavior.

## Bronsted-Lowry theory

We have been previously learned an Arrhenius acid-base theory which provided a good start towards the acid-base chemistry but it has certain limitations and problems. After this theory, a Danish chemist, named Johannes Nicolaus Bronsted and British scientist, Thomas Martin Lowry proposed a different definition of acid-base that based on the abilities of compound to either donate or accept the protons. This theory is known as Bronsted-Lowry theory, also called Proton theory of acid and base. This theory gives a more general and useful acid-base definition and applies to wide range of chemical reactions. In this theory, we usually consider a hydrogen atom as a proton that has lost its electrons and becomes a positively charged hydrogen ion (represented by symbol,  $H^+$ ).

According to Bronsted-Lowry concept, an acid is considered to be Bronsted-Lowry acid which is capable to donate a proton to someone else. A base is considered to be Bronsted-Lowry base which is capable to accept a proton from someone else. From here, it can note that when an acid reacts with a base, the proton is transferred from one chemical species to another.

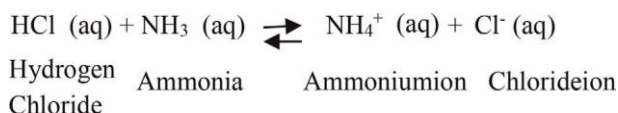
- Bronsted-Lowry acid-Hydrogen ion (Proton) donor.
- Bronsted-Lowry base-Hydrogen ion (Proton) acceptor.

## Conjugate acid-base pairs

- Conjugate acid: It forms when a base accepts proton.
- Conjugate base: It forms when an acid donates proton.

Note: If an acid is strong, the conjugate base will be weaker and if the base is strong, the conjugate acid will be weak.

Consider the following chemical reaction:



In this reaction, HCl is an acid because it is donating proton to  $NH_3$ . Therefore, HCl is act as Bronsted-Lowry acid whereas  $NH_3$  has a lone

pair of electrons which is used to accept the protons. Therefore,  $\text{NH}_3$  is act as Bronsted-Lowry base. This reaction is reversible also. In reversible case, the ammonium ion reacts with chloride ion and again converts into ammonia ( $\text{NH}_3$ ) and hydrogen chloride ( $\text{HCl}$ ). In this case, the ammonium ion is donating a proton, called conjugate acid. The chloride ion ( $\text{Cl}^-$ ) ion is accepting a proton, called conjugate base.

There are two conjugate pairs—conjugate pair 1 and conjugate pair 2.

Conjugate pair 1:  $\text{HCl}$  and  $\text{Cl}^-$

Conjugate pair 2:  $\text{NH}_3$  and  $\text{NH}^+$

From that equation, the ammonium ion ( $\text{NH}^+$ ) is a conjugate acid of base ammonia and chloride ion ( $\text{Cl}^-$ ) is a conjugate base of acid hydrogen chloride.

Note: According to the theory of Arrhenius, the reaction between  $\text{HCl}$  and  $\text{NH}_3$  is not considered as acid-base reaction because none of these species gives  $\text{H}^+$  and  $\text{OH}^-$  ions in water.

### Examples of Bronsted-Lowry acids and bases



In this reaction, the nitric acid donates a proton to the water, therefore it act as a Bronsted-Lowry acid. Since, water accepts a proton from nitric acid, so it is act as Bronsted-Lowry base. In this reaction, the arrow is drawn only to the right side which means that reaction highly favours the formation of products.



In this reaction, the water is losing its proton, becomes hydroxide ( $\text{OH}^-$ ) and donates its proton to the ammonia. Therefore, water is act as Bronsted-Lowry acid. Ammonia is accepting a proton from the water, forms ammonium ion ( $\text{NH}_4^+$ ).

Therefore, ammonia is act as Bronsted-Lowry base.

From the above two reactions, we can conclude that the water is Amphoteric in nature which means that it can act as both: Bronsted-Lowry acid and Bronsted-Lowry base.

### Advantages of Bronsted-Lowry theory

1. This theory is able to explain the acid-base behavior in aqueous and non-aqueous medium.
2. It explains the basic character of substances like  $\text{NH}_3$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{CO}_3$ , that is, which do not contain  $\text{OH}$  group but according to Arrhenius theory, they are not considered as bases.

3. It explains the acidic character of substances like  $\text{CO}_2$ ,  $\text{SO}_2$ , etc. which do not contain hydrogen ion group but according to Arrhenius theory, they are not considered as acids.
4. This theory also explains the acid-base behavior of ionic species.

### **Disadvantages of Bronsted-Lowry theory**

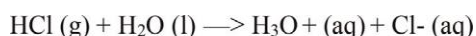
1. According to Bronsted-Lowry theory, same compound is act as acid in one reaction and act as base in other reaction. So, sometimes it is very difficult to predict the exact acid or base in a reaction.
2. This theory is not able to explain the acidic, basic as well as Amphoteric gaseous molecule.
3. This theory does not explain the behavior of acids like  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{BCl}_3$ , etc. which do not protons to loose or donate.
4. This theory does not explain reactions between acidic oxides ( $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ) and basic oxides ( $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{BaO}$ ) which takes place in the absence of solvent.

### **Relation between Arrhenius theory and Bronsted-Lowry theory**

These two theories are not against to each other in any way, in fact Bronsted-Lowry theory is advance to the Arrhenius theory.

According to the Arrhenius theory, a substance which produces hydrogen ion in water, called acid. A substance which produces hydroxide ion in water, called base.

According to Bronsted-Lowry theory, an acid is proton donor and base is proton acceptor.



According to Arrhenius theory, hydrochloric acid is an acid which gives hydro- gen ions in water but according to Bronsted-Lowry theory, hydrochloric acid is an acid because it donates a proton to the water molecule. By observing both concepts, water is acting as a base. So, we can see here that both theories are very similar to each other.

Actually, Arrhenius theory is limited only to the aqueous solution. It does not explain the acid behavior in gaseous form.

## **Lewis acid-base theory**

The Bronsted-Lowry theory which we have been previously studied was a good startup for acid-base chemistry. The Bronsted-Lowry concept was based on the transfer of proton from one chemical species to another. But this theory has certain limitations. UC Berkeley scientist, G.N. Lewis, in 1923 proposed a new acid-base theory which is based on their transfer of electrons. This theory is more advanced and flexible than Bronsted-Lowry because it explains the acid-base behavior in that molecules which do not contain hydrogen ions or in non-aqueous medium.

### **Lewis acid**

According to this theory, an acid is a substance which has capability to accept the non-bonding pair of electrons, called Lewis acid. They are sometimes referred as electron deficient species or electrophile.

#### *Lewis acid: characteristics*

- Lewis acid-electron-pair acceptor.
- Lewis acid should have a vacant or empty orbital.
- All cations ( $\text{Na}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ) are Lewis acids because they have capability to accept a pair of electrons but all Lewis acids are not cations.



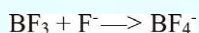
Metal cation having positive charge and empty orbital      Lone pair present on oxygen

More is the positive charge on the metal, more is the acidic character.  $\text{Fe}^{3+}$  is good Lewis acid than  $\text{Na}^+$ .

- The ion, molecule or an atom which has incomplete octet of electrons are also Lewis acids.

For example:  $\text{BF}_3$ .

Here, you can see that the central atom boron has six electrons in its outermost shell. So, it has ability to accept more electrons due to the presence of an empty orbital and hence, act as Lewis acid.



- The molecule in which the central atom has more than eight electrons ( $\text{SiF}_4, \text{SiBr}_4$ ), are also considered as Lewis acids.
- The molecule like  $\text{CO}_2, \text{SO}_2$ , etc. are also considered as Lewis acid. These types of molecules form multiple bond between the atoms of different electronegativity. In case of transition metal ions, the metal having more electronegativity makes stronger Lewis acids.
- Electron poor  $\pi$ : system is also considered as Lewis acids, for example,  $[\text{CH}_2=\text{CH}]^+$ , etc.

## Lewis base

A base is a substance which has capability to donate the electrons, called Lewis base. They are sometimes referred as electron rich species or Nucleophile.

*Lewis base: characteristics*

1. Lewis base-electron-pair donor
2. All metal anions ( $\text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-$ ) are Lewis base because they have ability to donate the electron but all Lewis bases are not anions.

3. The ion, molecule or an atom which having a lone pair of electrons, are also considered as Lewis base.
4. The electron-rich  $\pi$  system is also considered as Lewis bases, for example, benzene, ethene, etc.
5. The strength of the Lewis base can be increased by increasing the electronegativity.

### Example of Lewis acid-base

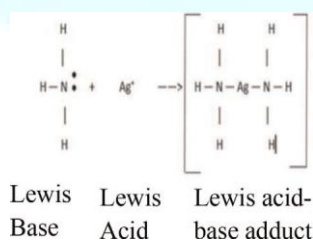
A simplest example of Lewis acid-base is shown by a chemical reaction:



In this reaction, chloride ion acts as Lewis base because it has lone pairs of electrons and sodium ion has positive charge, so it acts as Lewis acid.

### Neutralization reaction between Lewis acid and Lewis base

When a Lewis acid reacts with a Lewis base, then a Lewis acid-base reaction occurs in which the molecule which act as Lewis base donate its electron pair into the empty orbital of an acid, forms Lewis acid-base adduct. The adduct formed contains a covalent coordinate bond between Lewis acid and Lewis base. The above explanation implies that the Lewis acid is a low electron density centre and Lewis base is a high electron density centre.



*Acid-base neutralization.*

In this reaction, the two ammonia molecules reacts with silver ion. The ammonia has lone pair of electrons, so it has the ability to donate the lone pairs of electrons and acts as Lewis base. The positive charge on silver denotes its electrophilic nature that means it has an ability to

accept the pairs of electrons and act as Lewis acid (by Lewis definition).

Here, it can also be noted that when a Lewis acid reacts with a Lewis base, there is no change in the oxidation number of any of these atoms.

### **Limitations of Lewis acid-base theory**

1. This theory is not able to explain that why all acid-base reactions do not involve the covalent coordination bond.
2. This theory is also unable to explain the behavior of some acids like hydrogen chloride (HCl) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) because they do not form the covalent coordination bond with bases. Hence, they are not considered as Lewis acids.
3. This theory cannot explain the concept that why the formation of coordination bond is a slow process and acid-base reactions is a fast process.
4. This theory cannot explain the concept of relative strength of acids and bases.
5. This theory fails to explain the catalytic activity of some Lewis acids.

### **Relation between Lewis acid-base theory and Arrhenius theory**

1. All Arrhenius acids and Bronsted Lowry acids are Lewis acids but reverse is not true.

## NON-AQUEOUS SOLVENTS

Most of the chemical reactions familiar to us take place in aqueous solution since water, due to the high value of its dielectric constant, has an increased ability to dissolve the ionic compounds and many other substances. However there are many chemical reactions which cannot be carried out in aqueous solution but can be studied in a non-aqueous medium. A large number of non-aqueous solvents have been discovered in the last few years. These solvents have a sizable value of their dielectric constant and hence can dissolve many substances. Examples of such solvents are anhydrous liq.  $\text{NH}_3$ , liq.  $\text{SO}_2$ , anhydrous  $\text{HF}$ , liq.  $\text{N}_2\text{O}_4$ , etc.

### Classification of Solvents :

Solvents have been classified in a number of ways, depending on the properties of the solvents. The most convenient classification of solvents is based on the electrolytic characteristics of the solvents. This classification has been shown below:

1. **Non-ionising solvents** or Nonpolar liquids or Aprotic solvents: e.g. benzene, carbon tetrachloride.
2. **Ionising solvent or Polar liquids:**
  - a. **Protogenic:**
    - i. Protogenic (acidic solvents) Strong tendency to donate protons.  
e.g.  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{F}_2$ ,  $\text{CH}_3\text{COOH}$
    - ii. Protophilic (basic solvents) Strong affinity to accept protons.  
e.g. Liq.  $\text{NH}_3$ , Pyridine, Ethylene diamine
    - iii. Amphiprotic (amphoteric solvents) Can act both as acids or bases. e.g.  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$
  - b. **Non-protogenic:** e.g. liq.  $\text{SO}_2$ ,  $\text{BrF}_3$ ,  $\text{HgBr}_2$

### 1. Non-ionising solvents (Non-polar solvents):

These solvents are also called aprotic solvents or non-protic or non-protic solvents. These solvents have no hydrogen in their structure.

e.g.  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$ , etc. These solvents have very little dielectric constant. They dissolve non-polar substances.

### 2. Ionising solvents (Polar solvents):

Examples of such solvents are  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{F}_2$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{H}_2\text{O}$ , liq.  $\text{NH}_3$ , liq.  $\text{SO}_2$ , pyridine,  $\text{BrF}_3$ ,  $\text{HgBr}_2$ ,  $\text{CH}_3\text{OH}$  etc. Polar solvents have associated structures. Non-polar substances do not dissolve in these solvents because of the squeezing effect produced by their associated structure. However ionic and covalent polar substances dissolve in them. The dissolution of ionic substances is due to their greater solvation energy than the lattice energy of the salts. Several covalent substances dissolve forming H-bonds.

### Classification of Ionising Solvents:



## I. Protonic Solvents:

These solvents have hydrogen in their structure. These may be of the following types:

### A. Proto-genic solvents (Acidic solvents):

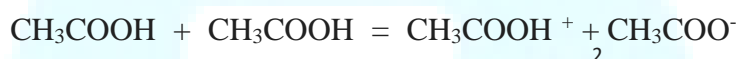
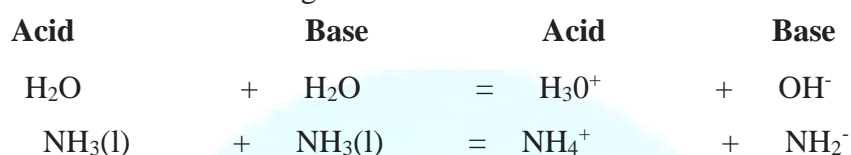
These solvents have a tendency to donate protons. e.g.  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{F}_2$ ,  $\text{CH}_3\text{COOH}$ .

### B. Protophilic solvents (Basic solvents):

These solvents have a tendency to accept protons. E.g. liq.  $\text{NH}_3$ , pyridine, ethylenediamine etc.

### C. Amphi-protic or amphoteric solvents:

These show dual character i.e. they can lose as well as accept protons, depending on the nature of the reacting species, e.g.  $\text{H}_2\text{O}$ , alcohols, liq.  $\text{NH}_3$ ,  $\text{CH}_3\text{COOH}$ , etc. Amphoteric solvents undergo auto-ionisation (self-ionisation) in which a proton transfer between two similar neutral molecules takes place and a cation-anion pair of the solvent is obtained e.g.



## II. Non-Protonic Solvents:

These solvents have nothing to do with protons.e.g. liq.  $\text{SO}_2$ ,  $\text{BrF}_3$ ,  $\text{HgBr}_2$ . Due to self-ionisation they also furnish cations and anions, similar to protonic solvents.

In this chapter we shall restrict our study on ionising solvents only. i.e. inwhich inorganic substances ionise and give ionic reactions as in  $\text{H}_2\text{O}$ . Non-ionising solvents are of great interest in organic chemistry.

## Physical Properties of Solvents and their Role in ChemicalReactions:

Every liquid cannot be used as a solvent in a chemical reaction.Here we compare the properties of some non-aqueous solvents with the properties of  $\text{H}_2\text{O}$ .

### 1. Melting point and boiling point:

Most of the chemical reactions are carried out in the liquid phase. Hencethe melting point and boiling point of a solvent indicates the range of temperature within which the solvent can be used. Melting points and boiling points( $^0\text{C}$ ) of some solvents are given below:

Solvent	Melting point	Boiling point	Characteristics
$\text{H}_2\text{O}$	0.0	100	Very convenient liquid

CH <sub>3</sub> COOH	16.16	118.1	Can act at ordinary temperature
NH <sub>3</sub>	-77.7	-33.4	Can act at low temperature
SO <sub>2</sub>	-75.5	-10.2	Can act at low temperature
HF	-89.3	19.5	----

### Dielectric constant ( $\epsilon$ ):

Dielectric constant ( $\epsilon$ ) of a solvent determine ability of the solvent to dissolve polar and non-polar substances in it. The coulombic force (F) between a cation and an anion of an ionic compound is given by the expression:

$$F = q_1 q_2 / \epsilon (r_1 + r_2)^2$$

In this expression  $q_1$  and  $q_2$  are the charges on cation and anion respectively,  $r_1$  and  $r_2$  are the radii of the two ions and  $\epsilon$  is the dielectric constant of the solvent. The value of  $\epsilon$  depends on the nature of the solvent in which the ionic compound is dissolved. The value of dielectric constant of some solvents are given below.

Solvent	Value of $\epsilon$	Solvent	Value of $\epsilon$
H <sub>2</sub> O	78.5 (25°C)	CH <sub>3</sub> COOH	9.7 (18°C)
NH <sub>3</sub>	22.0 (-33.5°C)	HF	83.6 (0°C)
SO <sub>2</sub>	17.3 (-16°C)	N <sub>2</sub> O <sub>4</sub>	2.42 (0°C)

It may be clear from the above expression that if  $\epsilon$  of a solvent is large, F would be small i.e. if  $\epsilon$  is large, small amount of energy would be required to separate the ions and hence it would be easy for a solvent having a high value of  $\epsilon$  to dissolve an ionic compound in it. For example, since anhydrous HF and H<sub>2</sub>O have high values of  $\epsilon$ , these are the best solvents for ionic compounds.

On the other hand, since liq.NH<sub>3</sub> and liq.SO<sub>2</sub> has low values of  $\epsilon$ , these solvents show smaller ability to dissolve ionic compounds especially those containing multi-charged ions. Thus carbonates, sulphates and phosphates which contain multi-charged ions are insoluble in liq.NH<sub>3</sub> and liq.SO<sub>2</sub>.

## 2. Dipole moment:

Greater is the polarity of the bond in a solvent molecule, greater is the charge separation and

higher will be the value for dipole moment. Substances having high dipole moment values are good solvent for polar solutes. This is because of the fact that greater is the polarity of a solvent molecule, greater is the solvation energy released on dissolution of a solute. Dipole moment value of a solvent also gives an idea about the extent of association of the molecules of a liquid and hence its liquid range. Dipole moment values (in D) of H<sub>2</sub>O, NH<sub>3</sub> and SO<sub>2</sub> are given below.

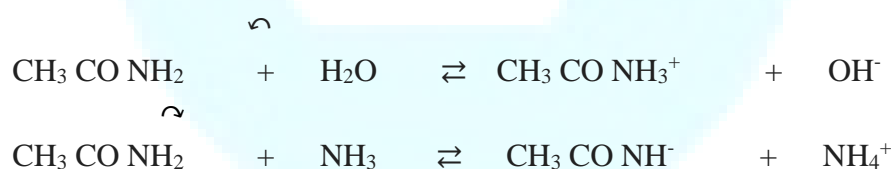
Solvent	H <sub>2</sub> O	NH <sub>3</sub>	SO <sub>2</sub>
Dipole moment	1.85	1.47	1.61

### 3. Viscosity:

Viscosity gives a measure of the fluidity of the solvent. Solvents like water, carbon tetrachloride have low viscosity and flow rapidly under ordinary temperature. In solvent of low viscosity, the operations such as precipitation, crystallization, filtration, etc. can be easily carried out without any difficulty. With increasing viscosity of a liquid, the difficulty of such operations increases. Solvents like anhydrous sulphuric acid have higher viscosities and this reduces their usefulness as solvent, Viscosity of H<sub>2</sub>O, NH<sub>3</sub> and SO<sub>2</sub> is 1.00, 0.241 and 0.009 respectively.

### 4. Proton affinity:

It is applicable for protonic solvents only. It greatly affects the behaviour of a solute in a given solvent. NH<sub>3</sub> has greater proton affinity than H<sub>2</sub>O. Hence acetamide (CH<sub>3</sub> CO NH<sub>2</sub>) which behaves as a very weak base in aqueous solution shows acidic properties in liq. NH<sub>3</sub>.



Proton affinity (in kJ mol<sup>-1</sup>) for H<sub>2</sub>O and NH<sub>3</sub> are 760 and 865 respectively. The properties of H<sub>2</sub>O, NH<sub>3</sub> and SO<sub>2</sub> other than those mentioned above are given below:

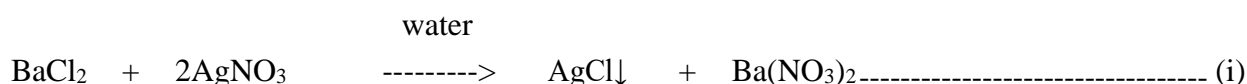
Property	H <sub>2</sub> O	NH <sub>3</sub>	SO <sub>2</sub>
Equivalent conductance (ohm <sup>-1</sup> )	6 x 10 <sup>-8</sup> (25°C)	5 x 10 <sup>-8</sup> (133.4°C)	1 x 10 <sup>-7</sup>
Critical temperature(°C)	374	132.4	157.5
Critical pressure	217.7	112.0	77.8

Density (g/cc)	0.96	0.68	1.46
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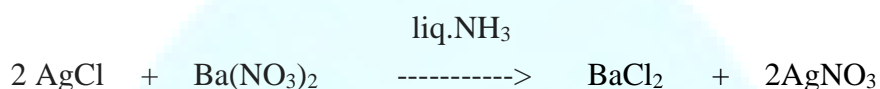
## Types of Chemical Reactions Taking Place in Non-aqueous Solvents:

### 1. Metathetical (Precipitation) Reactions

The reactions in which precipitate is formed by mixing two solutions of two compounds are called metathetical or precipitation reactions. Thus precipitation reactions are normally double decomposition. The formation of a precipitate in different solvents depends on the solubilities of the products in those solvents. For example the precipitate of AgCl is obtained by mixing BaCl<sub>2</sub> and AgNO<sub>3</sub> in aqueous medium.



In liq.NH<sub>3</sub> the above reaction is reversed, i.e., in liq.NH<sub>3</sub> ppt. of BaCl<sub>2</sub> is obtained by combining AgCl with Ba(NO<sub>3</sub>)<sub>2</sub>.



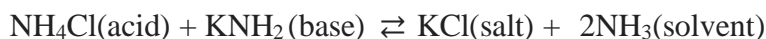
Thus we see that reaction (i) is reversed on changing the solvent.

### 2. Acid-Base Reactions

We have already said that the ionic solvents are polar compounds and undergo self-ionisation, Self-ionisation of some important solvents is given below:

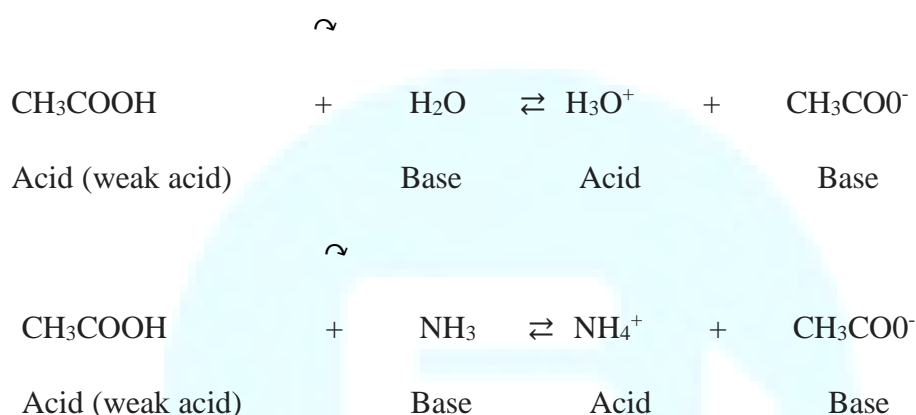
Solvent		Solvent cation (Acid ion)		Solvent anion (Base ion)
2H <sub>2</sub> O	⇌	H <sub>3</sub> O <sup>+</sup>	+	OH <sup>-</sup>
2NH <sub>3</sub>	⇌	NH <sub>4</sub> <sup>+</sup>	+	NH <sub>2</sub> <sup>-</sup>
2BrF <sub>3</sub>	⇌	BrF <sub>2</sub> <sup>+</sup>	+	BrF <sub>4</sub> <sup>-</sup>
2HgBr <sub>2</sub>	⇌	HgBr <sup>+</sup>	+	HgBr <sub>3</sub> <sup>-</sup>
2SO <sub>2</sub>	⇌	SO <sup>2+</sup>	+	SO <sub>3</sub> <sup>2-</sup>
2H <sub>2</sub> SO <sub>4</sub>	⇌	H <sub>3</sub> SO <sub>4</sub> <sup>+</sup>	+	HSO <sub>4</sub> <sup>-</sup>
CH <sub>3</sub> COOH	⇌	CH <sub>3</sub> COOH <sub>2</sub> <sup>+</sup>	+	CH <sub>3</sub> COO <sup>-</sup>
2HClO <sub>4</sub>	⇌	H <sub>2</sub> ClO <sub>4</sub>	+	ClO <sub>4</sub> <sup>-</sup>
3HF	⇌	H <sub>2</sub> F <sup>+</sup>	+	HF <sub>2</sub> <sup>-</sup>
N <sub>2</sub> O <sub>4</sub>	⇌	NO <sup>+</sup>	+	NO <sub>3</sub> <sup>-</sup>

An acid-base reaction in a non-aqueous solvent can be explained on the basis of the solvent system concept of acids and bases. According to this concept an acid is a substance which contains the solvent cation and a base is a substance which contains the solvent anion. For example since self-ionisation of liq.  $\text{NH}_3$ .



### Acidic character of $\text{CH}_3\text{COOH}$ in $\text{H}_2\text{O}$ and liq. $\text{NH}_3$ :

When  $\text{CH}_3\text{COOH}$  reacts with  $\text{H}_2\text{O}$  and liq.  $\text{NH}_3$  (solvents),  $\text{H}_2\text{O}$  and liq.  $\text{NH}_3$  both accept a proton from  $\text{CH}_3\text{COOH}$  to produce  $\text{H}_3\text{O}^+$  and  $\text{NH}_4^+$  ions. Due to the production of these ions,  $\text{CH}_3\text{COOH}$  behaves as an acid in both the solvents.



Now since the proton accepting ability of  $\text{H}_2\text{O}$  is less than that of liq.  $\text{NH}_3$ ,  $\text{CH}_3\text{COOH}$  behaves as weak acid in aqueous solution and acts as a strong acid in liq.  $\text{NH}_3$ .

### 3. Solvation Reactions: Formation of Solvates

Solvation reaction is a general reaction in which a solute (a cation, an anion or a neutral molecule) reacts with one or more molecules of a solvent (e.g.  $\text{H}_2\text{O}$ , liq.  $\text{NH}_3$ , liq.  $\text{SO}_2$  etc.) to form a product in which the solute and solvent species are attached to each other by a H-bond or by a coordinate bond. The product formed is called **solvate**. Solvate is an addition compound and hence is also called an **adduct**. The addition compound contains **solvent of crystallisation**.

In the formation of a solvate, the solvent acts as a Lewis base while the solute species behaves as a Lewis acid. When the solvent used is water, the solvation reaction is called **hydration** and the addition compound formed is called **hydrate**. Hydrate contains one or more molecules of water as water of crystallisation. Similarly when the solvent is liq.  $\text{NH}_3$ , the reaction is called **ammoniation** and the addition compound formed is called **ammoniate**. Ammoniate contains one or more molecules of ammonia as **ammonia of**

crystallisation.

#### 4. Solvolytic Reactions: Solvolysis

Solvolytic reactions are the reactions in which the solvent molecules react with the solute molecule (salt) or ion in the way which consists of the following steps:

- (a) The solvent molecule undergoes auto-ionisation (self-ionisation) to give solvent cations and solvent anions.
- (b) The solute (salt) splits into solute cations and solute anions. The solute cations or solute anions interact with the solvent cations or solvent anions. Due to this interaction the concentration of the solvent cations or solvent anions is increased. When  $\text{H}_2\text{O}$  and  $\text{NH}_3$  are used as solvents in the solvolytic reactions, the reactions are called **hydrolysis and ammonolysis (or ammonolysis reactions)** respectively.

#### Liquid Ammonia (Liq. $\text{NH}_3$ ) Solubility of Various Substances in

##### Liq. $\text{NH}_3$ :

#### A. Solubility of ionic compounds (inorganic salts):

We know that ammonia has a low value of its dielectric constant ( $\epsilon = 22$  at  $-34^\circ\text{C}$ ). This low value suggests that liq.  $\text{NH}_3$  has a poor ability to dissolve ionic compounds. Ammonium salts (e.g.  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{SCN}$ ,  $\text{CH}_3\text{COONH}_4$  etc.) and most of the nitrites, nitrates, cyanide, thiocyanate, perchlorates, are soluble in liq.  $\text{NH}_3$ . Salts containing highly charged ions (e.g., oxides, sulphides, sulphates, phosphates and carbonates) are insoluble. Fluorides and chlorides (except  $\text{Be}^{2+}$  and  $\text{Na}^+$  chlorides) are practically insoluble, bromides are less soluble while iodides are freely soluble. Thus the solubility of the halides of a given metal increases in going from fluoride to iodide ( $\text{MF} < \text{MCl} < \text{MBr} < \text{MI}$ ).

Most of the metal amides (except those of alkali metals) are insoluble. The salts of some metals (e.g.  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  etc.) react with liq.  $\text{NH}_3$  and form ammine complexes.

#### B. Solubility of non-ionic compounds (organic compounds):

Halogen compounds, alcohols, ketones, esters, simple ethers, amines, phenol and its derivatives etc. are soluble. Alkanes are insoluble and alkenes and alkynes are slightly soluble. In this sense, liq.  $\text{NH}_3$  is a better solvent for non ionic and nonpolar compounds (organic compounds).

#### C. Solubility of non-metals:

The non-metals like S, P,  $\text{I}_2$ , Se etc. are soluble and they react with the solvent.

## D. Solubility of alkali metals and alkaline earth metals:

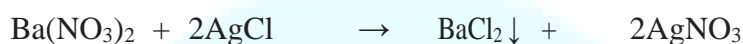
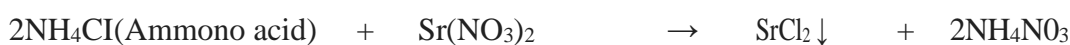
All the alkali metals and alkaline earth metals (excepting Be) are soluble in liq.  $\text{NH}_3$ . 100g of liq.  $\text{NH}_3$  dissolves 10.9g of Li, 24.8g of Na, 46.8g of K (all at  $-33^\circ\text{C}$ ) and 334g of Cs (at  $-50^\circ\text{C}$ ). Thus we see that the solubility of alkali metals in liq.  $\text{NH}_3$  increases as we pass from Li to Cs ( $\text{Li} < \text{Na} < \text{K} < \text{Cs}$ ).

## Chemical Reactions Taking Place in Liq. $\text{NH}_3$

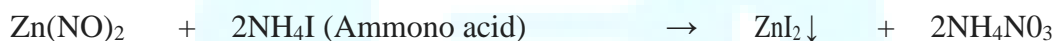
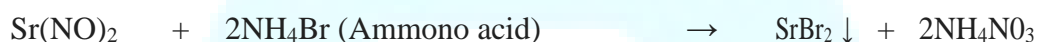
### 1. Metathetical (Precipitation) Reactions

Examples of some precipitation reactions taking place in liq.  $\text{NH}_3$  are given below.

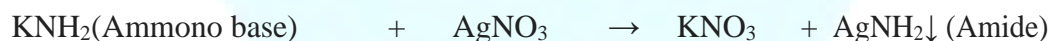
#### a. Chlorides are precipitated:



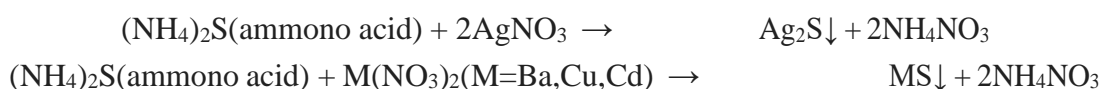
#### b. Bromides and iodides are precipitated:



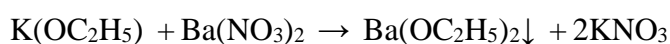
#### c. Amides ( $\text{NH}_2^-$ ), imides ( $\text{NH}^{2-}$ ) and nitrides ( $\text{N}^{3-}$ ) can be precipitated:



#### d. Sulphides are precipitated:

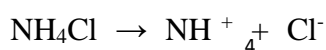


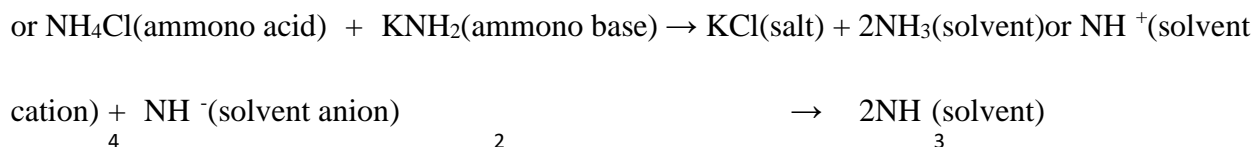
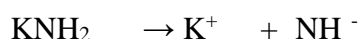
#### e. Barium alcoholate can be precipitated:



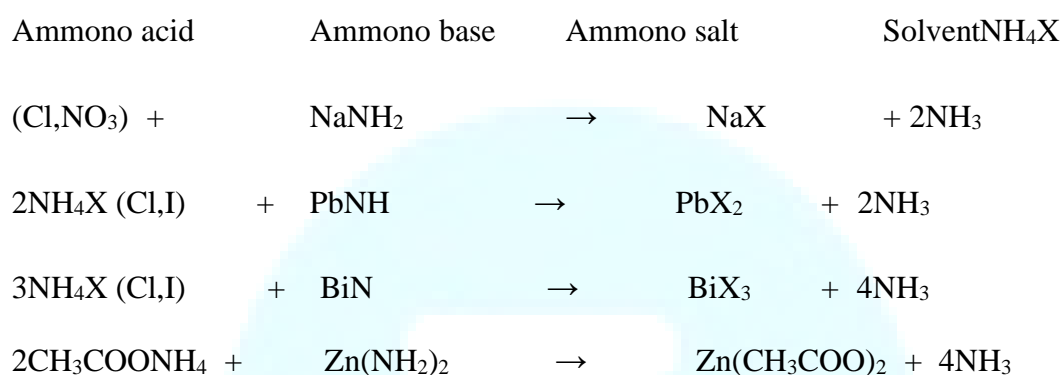
### 2. Acid-base Neutralisation reaction (salt formation) reactions

A compound containing or making available  $\text{NH}^+$  or  $\text{NH}_2^-$  or  $\text{N}^{3-}$  ion (ammono base) to form the salt and the solvent  $\text{NH}_3$ .



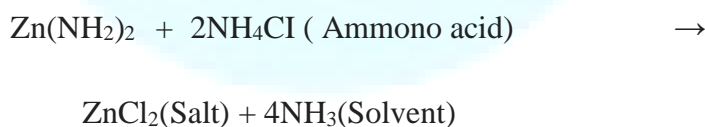


Above equation indicates that neutralisation reaction in liq.  $\text{NH}_3$  can also be defined as the combination of solvent cation ( $\text{NH}_4^+$ ) and solvent anion ( $\text{NH}_4^-$ ) to form the un-ionised solvent (liq.  $\text{NH}_3$ ). Other examples in liq.  $\text{NH}_3$  are:

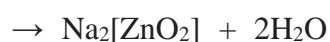
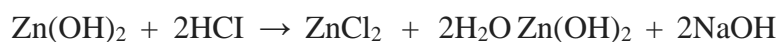


### 3. Amphoteric Behaviour of $\text{Zn}(\text{NH}_2)_2$ in Liq. $\text{NH}_3$ :

$\text{Zn}(\text{NH}_2)_2$  dissolves in ammono acid as well as in ammono base in liq.  $\text{NH}_3$  and hence is said to show amphoteric character in liq.  $\text{NH}_3$ .



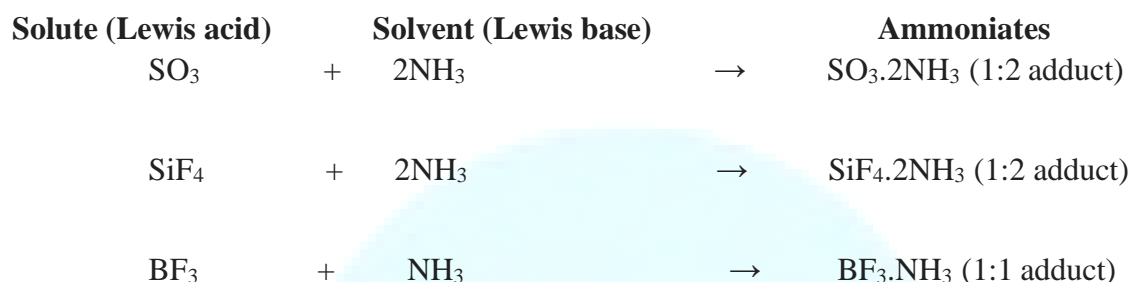
Above reactions can be compared with the following reactions in aqueous solution. In these reactions  $\text{Zn}(\text{OH})_2$  shows amphoteric character since it dissolves in  $\text{HCl}$  (acid) as well as in  $\text{NaOH}$  (base).





#### 4. Ammonation Reaction : Formation of Ammoniates (Solvation Reactions - Formation of Solvates):

Solvation reaction in which liq.  $\text{NH}_3$  is used as solvent is called **ammonation reaction** and the solvate formed is called **ammoniate**. In the formation of ammoniate liq.  $\text{NH}_3$  (solvent) acts as a Lewis base and the solute behaves as a Lewis acid. The formation of some ammoniates in liq.  $\text{NH}_3$  has been shown below. These ammoniates may be 1 : 2 or 1 : 1 adducts.



The formation of  $\text{NH}_4^+$  by action of liq.  $\text{NH}_3$  on  $\text{H}_2\text{O}$  is also an example of ammoniation. More examples of ammoniates formed by liq.  $\text{NH}_3$  with inorganic salts are  $\text{MgI}_2 \cdot 6\text{NH}_3$ ,  $\text{NiI}_2 \cdot 6\text{NH}_3$ ,  $\text{NaI} \cdot 4\text{NH}_3$  etc. In the formation of these ammoniates,  $\text{NH}_3$  molecules (solvent molecules) are coordinated to the metal ions of the inorganic salt (solute).

#### 5. Ammonolysis or Ammonolytic Reaction : (Solvolysis or Solvolytic Reactions)

The solvolytic reactions taking place in aqueous medium ( $\text{H}_2\text{O}$ ) and liq.  $\text{NH}_3$  are called hydrolysis and ammonolysis (or ammonolytic reactions) respectively. In hydrolysis  $\text{H}_2\text{O}$  is used as a solvent while in ammonolysis liq.  $\text{NH}_3$  is used as a solvent.

##### Examples of ammonolysis:

##### a. Ammonolysis of $\text{SnCl}_4$ , $\text{SiCl}_4$ and $\text{SO}_2\text{Cl}_2$ :

In the ammonolysis of  $\text{SnCl}_4$  and  $\text{SO}_2\text{Cl}_2$  (solute) the concentration of  $\text{NH}_4^+$  (solvent cations) is increased as shown below:



On adding:  $\text{SnCl}_4(\text{Solute}) + 8 \text{NH}_3(\text{Solvent}) \rightarrow \text{Sn}(\text{NH}_2)_4 + 4\text{Cl}^- + 4\text{NH}_4^+$



**b. Ammonolysis of alkali metal hydrides and oxides:**

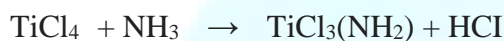
The ammonolysis of alkali metal hydrides and oxides gives alkali metal amides ( $\text{MNH}_2$ ). In these reactions the concentration of  $\text{NH}_2^-$  ions (solvent anions) is increased..

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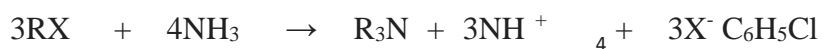
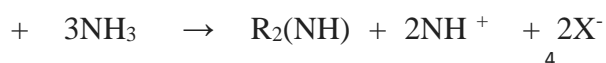
**c. Ammonolysis of  $\text{TiCl}_4$ :**

Ammonolysis of  $\text{TiCl}_4$  (salt) in presence of excess of liq.  $\text{NH}_3$  produces  $\text{Ti}(\text{NH}_2)_4$ . In each step Cl-atom of the salt undergoing ammonolysis is replaced by  $-\text{NH}_2$  group.



**d. Ammonolysis of alkyl and aryl halides:**

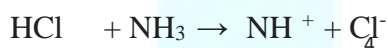
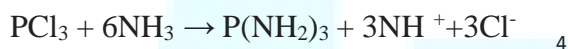
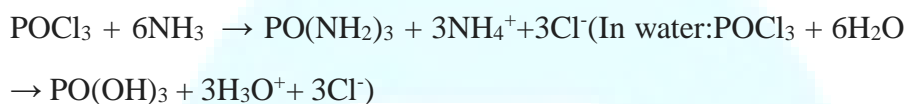
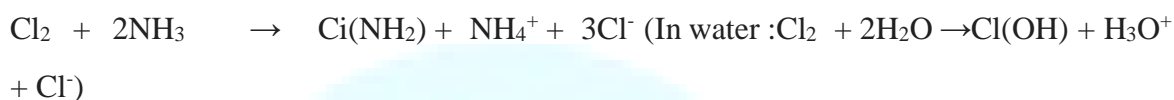
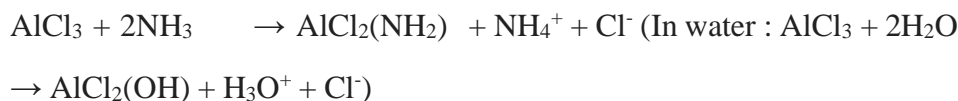
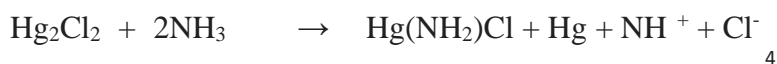
The ammonolysis of alkyl halides  $\text{RX}$  ( $\text{R}$  = alkyl group,  $\text{X} = \text{Cl, Br, I}$ ) takes place slowly at the boiling point of liq.  $\text{NH}_3$ . In this reaction mixture of primary ( $\text{RNH}_2$ ) secondary ( $\text{R}_2\text{NH}$ ) and tertiary ( $\text{R}_3\text{N}$ ) amines is obtained.



4

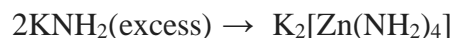
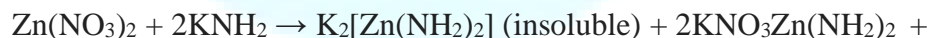
**e. Ammonolysis reactions:**

In all these reactions the concentration of  $\text{NH}_4^+$  is increased.



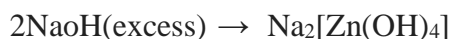
**6. Complex Formation Reactions:**

- a.** Many metal salts (e.g.  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{AlCl}_3$ , etc.) react with excess of  $\text{KNH}_2$  solution in **liq  $\text{NH}_3$**  to form soluble amido complexes. For example:

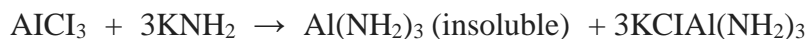


**On adding:**  $\text{Zn}(\text{NO}_3)_2 + 4\text{KNH}_2 \rightarrow \text{K}_2[\text{Zn}(\text{NH}_2)_4] \text{ (soluble)} + 2\text{KNO}_3$  Above reaction

that occurs in **aqueous ( $\text{H}_2\text{O}$ )** medium.

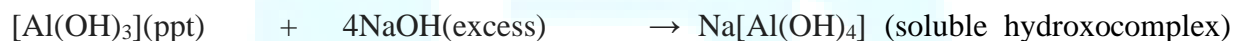


**On adding:**  $\text{Zn(NO}_3)_2 + 4\text{NaOH} \rightarrow \text{Na}_2[\text{Zn(OH)}_4] \text{ (soluble amidocomplex) } + 2\text{NaNO}_3$



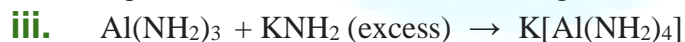
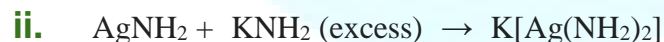
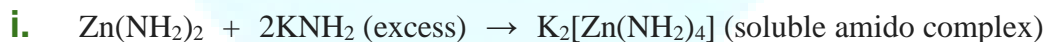
**On adding:**  $\text{AlCl}_3 + 4\text{KNH}_2 \rightarrow \text{K[Al(NH}_2)_4] \text{ (soluble amido complex) } + 3\text{KCl}$

This reaction can be compared with the reaction of  $\text{AlCl}_3$  with **excess of NaOH** taking place in aqueous solution.



**On adding:**  $\text{AlCl}_3 + 4\text{NaOH}(\text{excess}) \rightarrow 3\text{NaCl} + \text{Na[Al(OH)}_4]$

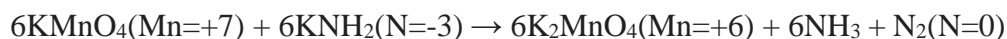
**b.** Many metal amides, imides and nitrides dissolve in the excess of  $\text{KNH}_2$  in liq.  $\text{NH}_3$  to form soluble amido complexes. For example



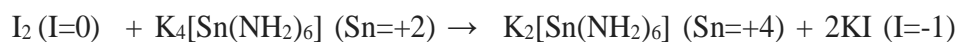
## 7. Redox Reactions:

**a. Redox reactions in which liq.  $\text{NH}_3$  serves as a medium only.**

**i.**  $\text{KMnO}_4$  acts as a weak oxidising agent in liq.  $\text{NH}_3$ . It oxidises  $\text{KNH}_2$  to  $\text{N}_2$  in liq.  $\text{NH}_3$  and is itself reduced to  $\text{K}_2\text{MnO}_4$ .



- ii. Iodine also acts as a weak oxidising agent in liq.  $\text{NH}_3$ . It oxidises potassium ammonostannite,  $\text{K}_4[\text{Sn}(\text{NH}_2)_6]$  to potassium ammonostannate,  $\text{K}_2[\text{Sn}(\text{NH}_2)_6]$  and is itself reduced to KI.



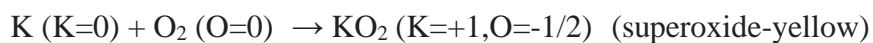
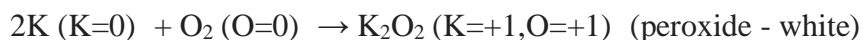
**b. Redox reactions in which liq.  $\text{NH}_3$  (N= -3, H = +1) itself acts as a reducing agent:**

- i.  $4\text{NH}_3 (\text{N}=-3) + 5\text{O} (\text{O}=0) \rightarrow 4\text{NO} (\text{N}=+2) + 6\text{H}_2\text{O} (\text{O}=-2)$
- ii.  $2\text{NH}_3 (\text{N}=-3) + 3\text{CuO} (\text{Cu}=+2) \rightarrow \text{N}_2 (\text{N}=0) + 3\text{Cu} (\text{Cu}=0) + 3\text{H}_2\text{O}$

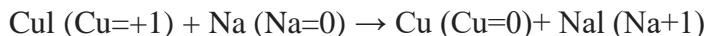
**c. Redox reactions in which alkali metals in liq.  $\text{NH}_3$  act as reducing agents:**

Liq.  $\text{NH}_3$  can dissolve the alkali metals in it. The solution thus obtained contains ammoniated electrons. These electrons reduce various substances. Thus alkali metals in liq.  $\text{NH}_3$  are able to reduce a variety of substances and are themselves oxidised to some alkali metal salt.

- i. Sodium in liq.  $\text{NH}_3$  reduces ammonium salt to  $\text{H}_2$
- $$2\text{Na} (\text{Na}=0) + 2\text{NH}_4\text{Br} (\text{H}=1) \rightarrow 2\text{NaBr} (\text{Na}=+1) + \text{H}_2 (\text{H}=0)$$
- ii. Potassium in liq.  $\text{NH}_3$  reduces nitrous oxide ( $\text{N}_2\text{O}$ ) to  $\text{N}_2$
- $$2\text{K} (\text{K}=0) + \text{NH}_3 + \text{N}_2\text{O} \rightarrow \text{KNH}_2 (\text{K}=+1) + \text{KOH} + \text{N}_2 (\text{N}=0)$$
- iii. Sodium in liq.  $\text{NH}_3$  reduces elemental sulphur to sodium sulphide ( $\text{Na}_2\text{S}$ )
- $$\text{S} (\text{S}=0) + 2\text{Na} (\text{Na}=0) \rightarrow \text{Na}_2\text{S} (\text{Na}=+1, \text{S}=-2)$$
- iv. Li and Na in liq.  $\text{NH}_3$  reduce elemental oxygen to their peroxide, while other alkali metals give their peroxide ( $\text{M}_2\text{O}_2$ ) as well as superoxide ( $\text{MO}_2$ ).



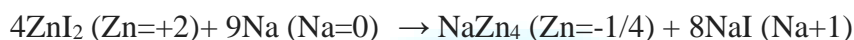
**v.** Na in liq.  $\text{NH}_3$  reduces  $\text{CuI}$  to  $\text{Cu}$



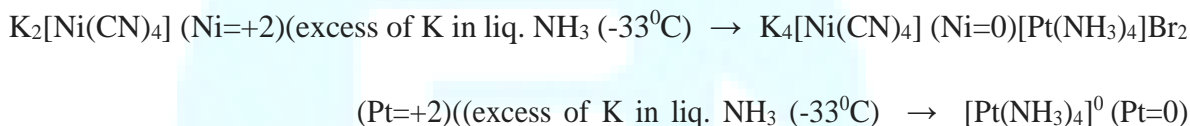
**vi.** K in liq.  $\text{NH}_3$  reduces  $\text{KMnO}_4$  to  $\text{MnO}$  and is itself oxidised to  $\text{KNH}_2$ .



**vii.** Na in liq.  $\text{NH}_3$  reduces  $\text{ZnI}_2$  to  $\text{NaZn}_4$  and is itself oxidised to  $\text{NaI}$ .

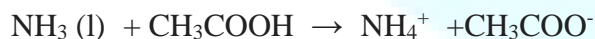


**viii.** Excess of K in liq.  $\text{NH}_3$  reduces  $\text{K}_2[\text{Ni}(\text{CN})_4]$  and  $[\text{Pt}(\text{NH}_3)_4]\text{Br}_2$  to  $\text{K}_4[\text{Ni}(\text{CN})_4]$  and  $[\text{Pt}(\text{NH}_3)_4]^0$  respectively.



## 8. Dissociation of Weak Acids by Liq. $\text{NH}_3$ :

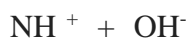
Since liq.  $\text{NH}_3$  has strong proton accepting ability, it accepts a proton from weak acids like  $\text{CH}_3\text{COOH}$ .



$\text{CH}_3\text{COOH}$  is completely ionised in liq.  $\text{NH}_3$  and hence acts as a strong acid in liq.  $\text{NH}_3$ .

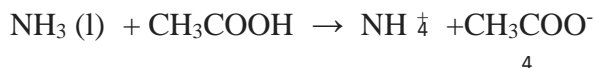
## 9. Reactions in Which $\text{NH}_3$ accepts a Proton : Pyrolysis :

$\text{NH}_3$  is a powerful proton acceptor to form  $\text{NH}^+$  ion. For example:

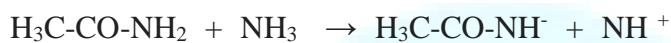
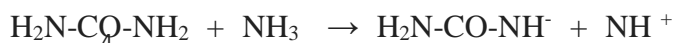


The high solubility of  $\text{NH}_3$  in  $\text{H}_2\text{O}$  is due to the above reaction

- b.  $\text{CH}_3\text{COOH}$  is a weak acid in  $\text{H}_2\text{O}$  but shows strong acidic character in  $\text{liq.NH}_3$  because  $\text{NH}_3$  picks up a proton from  $\text{CH}_3\text{COOH}$  to form  $\text{NH}^+$  ion.



- c. Urea ( $\text{NH}_2\text{CONH}_2$ ) and acetamide ( $\text{CH}_3\text{CONH}_2$ ) are weakly basic in aqueous solution but show acidic properties in  $\text{liq. NH}_3$  since these compounds can donate a proton to  $\text{NH}_3$  to produce  $\text{NH}^+$  ion.

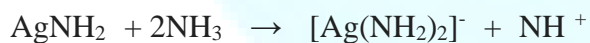


- d. Sulphonic acid ( $\text{NH}_2\text{SO}_2\text{OH}$ ) behaves as a dibasic acid in  $\text{liq. NH}_3$   $\text{H}_2\text{N}-\text{SO}_2-\text{OH} + 2\text{NH}_3$   
 $\rightarrow \text{HN}^--\text{SO}_2-\text{O}^- + 2\text{NH}^+$

Here it may be noted that  $\text{NH}_2\text{SO}_2\text{OH}$  acts as a monobasic acid in aqueous solution, since only the OH group present in this compound donates a proton to  $\text{H}_2\text{O}$ .



- e.  $\text{AgNH}_2$  behaves as a weak base in aqueous solution but in  $\text{liq.NH}_3$  it behaves as an acid.



In all the above examples concentration of  $\text{NH}_4$  increased. Hence, according to Cady and Esley concept of acids and bases, all these substances behave as acids in  $\text{liq.NH}_3$ .

### Advantages of Using Liquid Ammonia as a Solvent:

1. All the alkali metals, without reacting with  $\text{liq. NH}_3$ , is soluble in this solvent. The dissolved alkali metals can be recovered by evaporating the alkali metal- $\text{liq.NH}_3$  solution.
2. The alkali metal- $\text{liq NH}_3$  solution contains ammoniated electrons and hence these solutions act as strong reducing agents.



3. The study of precipitation reactions taking place in  $\text{liq.NH}_3$  these reactions can be used to precipitate metallic halides, sulphides, alcoholates, amide, imide and nitrides.

### Disadvantages of Using Liquid Ammonia as a Solvent :

1. Low temperature or high pressure is necessary while working with  $\text{liq.NH}_3$ . This is because of the fact that the liquid range for  $\text{liq.NH}_3$  is from  $-34.0^\circ\text{C}$  to  $-77.7^\circ\text{C}$ .
2.  $\text{Liq. NH}_3$  is hygroscopic in nature and hence all the reaction must be carried out in a sealed tube.
3.  $\text{Liq, NH}_3$  has an offensive odours and hence the use of  $\text{liq.NH}_3$  as a solvent and as a reaction medium requires special technique.

### Liquid Sulphur Dioxide ( $\text{Liq.SO}_2$ )

**Introduction:**  $\text{Liq.SO}_2$  is a non-protonic solvent, because it cannot give a proton on self ionisation. Under normal temperature and pressure, sulphur dioxide is a gas but can be readily liquefied. It has a wide liquid range from

$-10.0^\circ\text{C}(\text{b.p.})$  to  $-75.5^\circ\text{C}(\text{m.p.})$  and hence can be used as a solvent. Its dielectric constant is low ( $=17.4$  at  $-20^\circ\text{C}$ ) and hence it is poor solvent for ionic compounds but acts as a good solvent for covalent compound.

### Solubility of various substances in $\text{liq.SO}_2$ :

#### A. Solubility of ionic compounds (inorganic salts):

Iodide and thiocyanates : **Most soluble** Sulphates, sulphides, oxides and hydroxides :

**Partially insoluble** Ammonium, thallium and mercuric salts : **Soluble**

#### B. Solubility of non-ionic compounds (covalent compound) :

Covalent halide like  $\text{IBr}$ ,  $\text{BCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{AsCl}_3$ ,  $\text{PBr}_3$ ,  $\text{CCl}_4$ ,  $\text{SiCl}_4$  and  $\text{SnCl}_4$  :

**Soluble**

Organic compound like amines, ether, alcohols, benzene, alkenes, pyridine, quinoline, Halogen derivatives and acid chlorides : **Soluble** Alkanes : **Insoluble**

#### C. Solubility of metals:

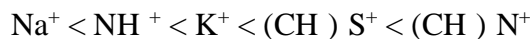
Metals are insoluble in  $\text{liq.SO}_2$

#### D. Conductivity of salt solution:

Conductivity of electrolyte solution of salt containing

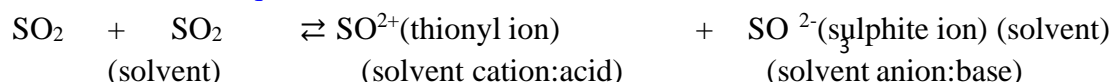
$\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $(\text{CH}_3)_4\text{S}^+$  and  $(\text{CH}_3)_4\text{N}^+$  increase with the increase in the size of these cations.

Increasing order of conductivity :



Size of anions in increasing order of conductivity:  $\text{SCN}^- < \text{ClO}_4^- < \text{Cl}^- < \text{I}^-$

**Auto-Ionisation of liq.  $\text{SO}_2$  :**

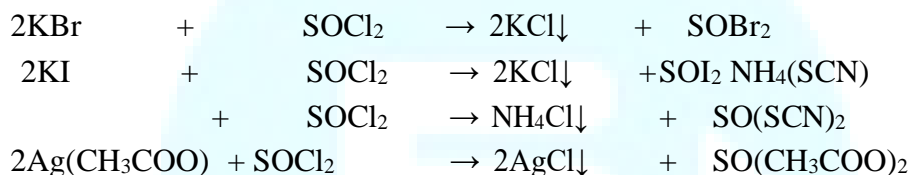


Compare the self ionisation of liq.  $\text{SO}_2$  with water and liq.  $\text{NH}_3$ :  $\text{SO}^{2+}$  ion analogous to  $\text{H}_3\text{O}^+$  and  $\text{NH}_4^+$  ions while  $\text{SO}_3^{2-}$  ion is analogous to  $\text{OH}^-$  and  $\text{NH}_2^-$  ions produced by the self-ionisation of  $\text{H}_2\text{O}$  and liq.  $\text{NH}_3$  respectively.

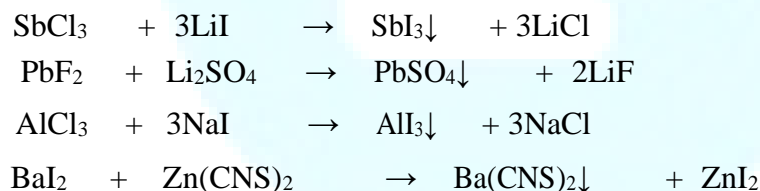
**Chemical reaction taking place in Liq.  $\text{SO}_2$  :**

### 1) Metathetical (Precipitation) Reaction:

a) Thionyl chloride ( $\text{SO}_2\text{Cl}_2$ ) in liq.  $\text{SO}_2$  has helped to prepare many compounds.



b) Some other reaction precipitation reaction that carried out in liq.  $\text{SO}_2$ :



### 2) Acid-Base neutralisation (salt formation) reaction:

In these reactions compounds contain  $\text{SO}^{2+}$  ion(acid) combined with compounds containing  $\text{SO}_3^{2-}$  ion(base) to form the salt and the solvent (liq.  $\text{SO}_2$ ). E.g.

a)  $\text{SOCl}_2(\text{acid}) + \text{Cs}_2\text{SO}_3(\text{base}) \rightarrow 2\text{CsCl}(\text{salt}) + 2\text{SO}_2(\text{solvent})$

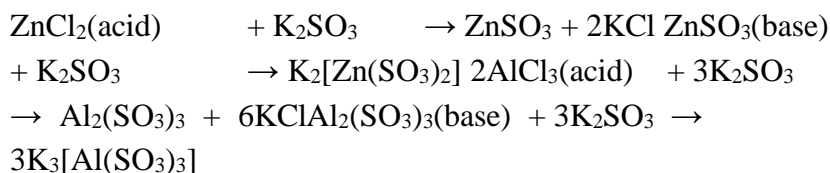


b)  $\text{SO}(\text{SCN})_2 + \text{K}_2\text{CO}_3 \rightarrow 2\text{K}(\text{SCN}) + 2\text{SO}_2$

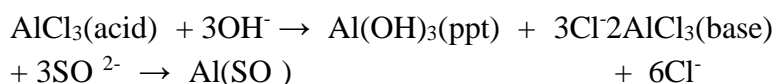
c)  $\text{SOBr}_2 + [\text{N}(\text{CH}_3)_4]_2\text{SO}_3 \rightarrow 2[\text{N}(\text{CH}_3)_4]\text{Br} + 2\text{SO}_2$

### 3) Amphoteric behavior of salts in liq. $\text{SO}_2$ :

a) Acidic and basic character with salts of Zn(II) and Al(III)



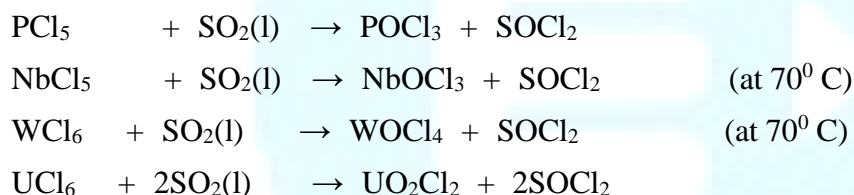
b) Acidic and basic behavior with  $\text{AlCl}_3$  and  $\text{GaCl}_3$



#### 4) Solvation Reactions : Formation of Solvates:

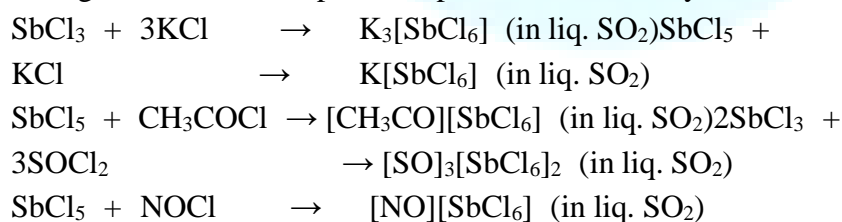
Like water and liq.  $\text{NH}_3$ , liq.  $\text{SO}_2$  also form addition compounds (solvates) with solutes. E.g.  $\text{LiI} \cdot 2\text{SO}_2$ ,  $\text{KBr} \cdot 4\text{SO}_2$ ,  $\text{M} \cdot 4\text{SO}_2$  ( $\text{M} = \text{Na}, \text{K}, \text{Rb}$ ),  $\text{M} \cdot 2 \cdot 4\text{SO}_2$  ( $\text{M} = \text{Ca}, \text{Ba}, \text{Sr}$ ),  $\text{AlCl}_3 \cdot 2\text{SO}_2$

#### 5) Solvolytic or solvolysis reaction:



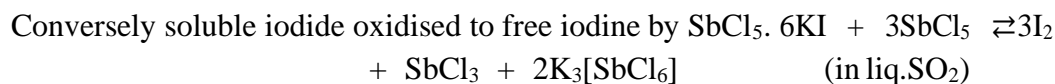
#### 6) Complex formation reaction:

A large number of complex compounds is formed by  $\text{SbCl}_3$  and  $\text{SbCl}_5$  in liq.  $\text{SO}_2$ .



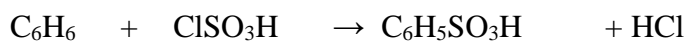
#### 7) Redox reaction:

Liq.  $\text{SO}_2$  does not have any strong oxidising or reducing properties, although it may serve as a medium for redox reaction. It reduced iodine but not bromine.



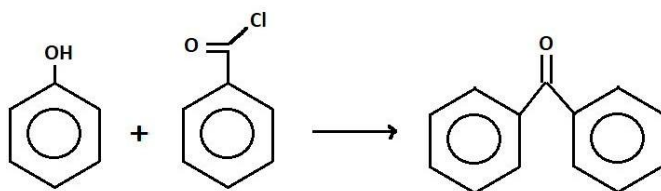
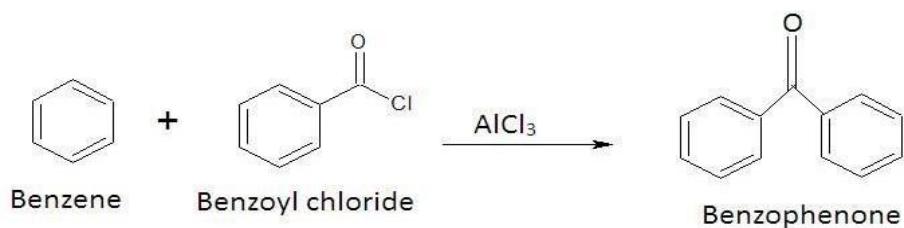
### 8) Reactions with Organic compounds:

a) Hydrocarbons undergo sulfonation in liq.  $\text{SO}_2$  :

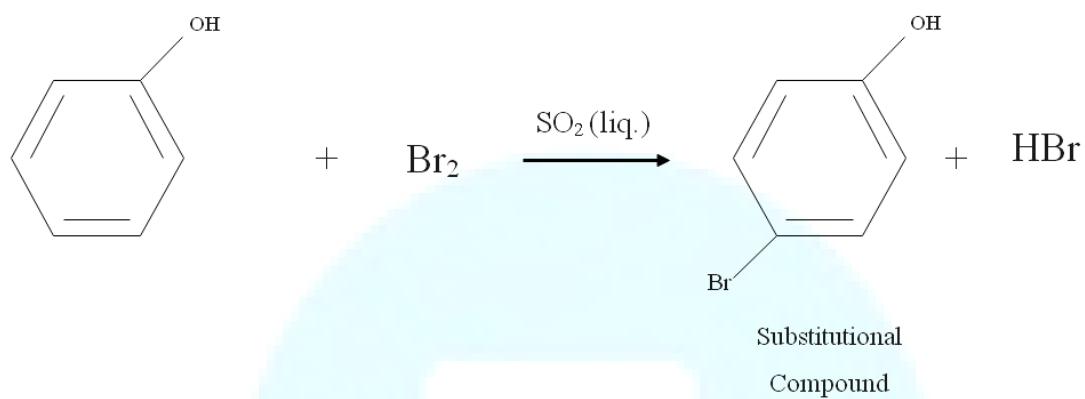
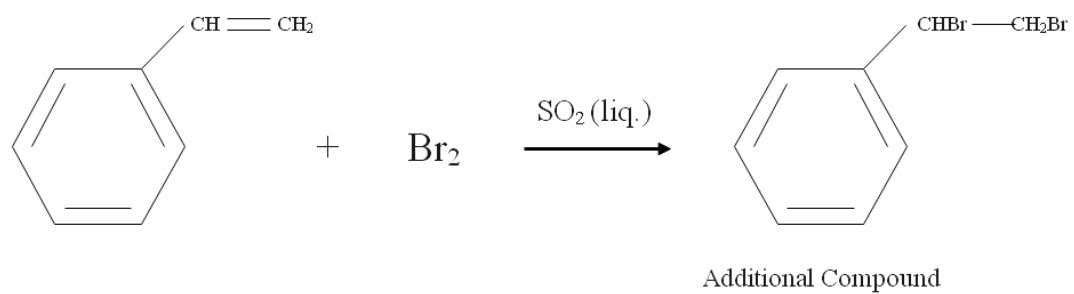


b) Friedel-Craft's reaction :

$\text{AlCl}_3$  which is used as a catalyst and reaction carried out in liq.  $\text{SO}_2$  medium.



c) Bromination: Liq.  $\text{SO}_2$  is also used as a solvent in various Bromination reactions.

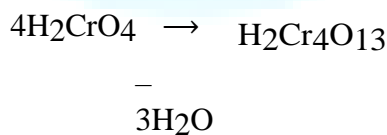
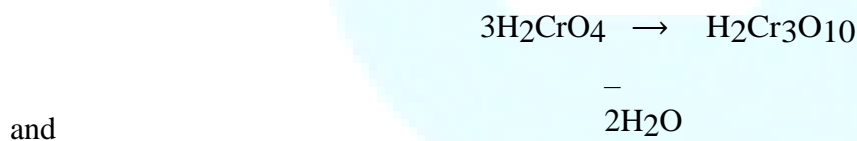


## Isopoly and Heteropoly Acids

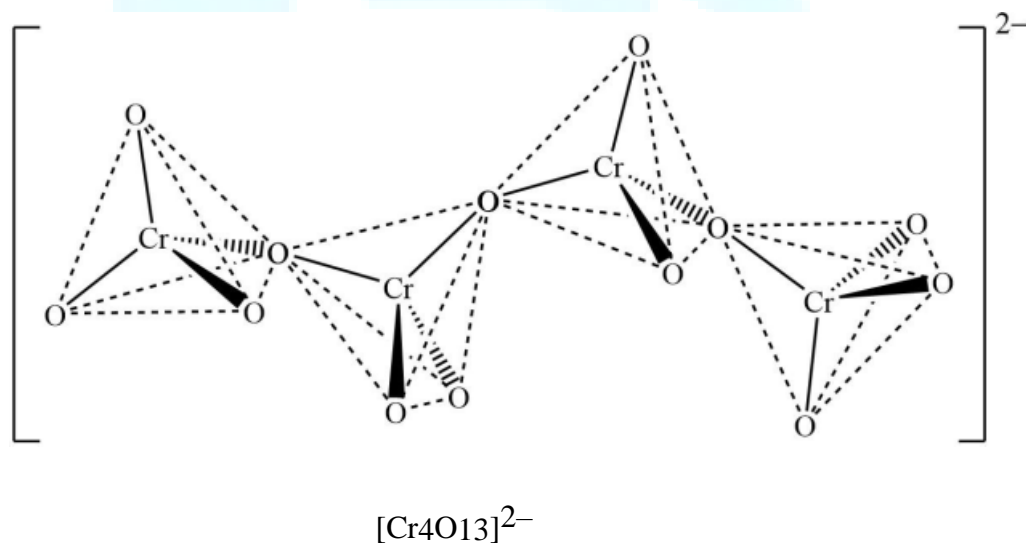
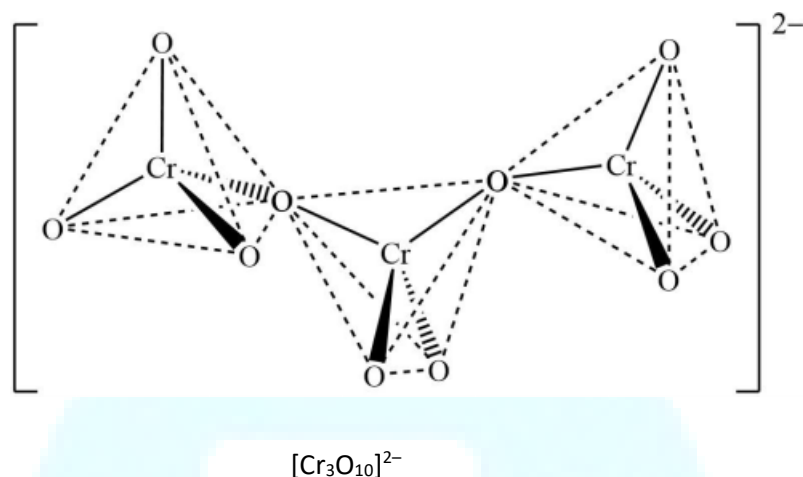
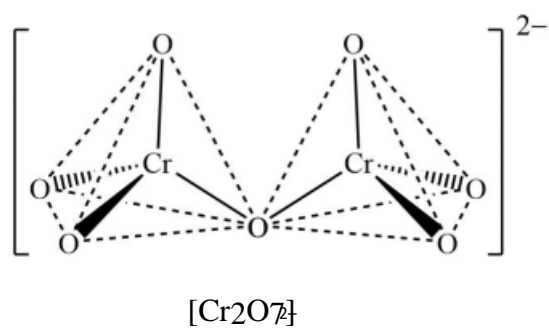
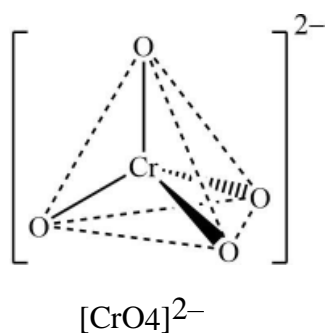
The term polymetalate acid or simply poly acid may be defined as the condensed or polymerized form of the weak acids of amphoteric metals like vanadium, niobium, tantalum (VB group metals) or chromium, molybdenum, and tungsten (VIB group metals) in the +5 and +6 oxidation states. The anions of these poly acids contain several molecules of the acid anhydride and the corresponding salts are called as polysalts.

Furthermore, if these polymerized acids contain only one type of acid anhydride, they are called as isopoly acids. However, these anhydrides can also condense with some other acids like phosphoric or silicic acid to form heteropoly acids. In other words, isopoly acids contain only one metal along with hydrogen and oxygen while heteropoly acids contain two elements other than hydrogen and oxygen. The corresponding salts of isopoly and heteropoly acids are called as isopoly and heteropoly salts, respectively.

Consider the polymerization of chromate ion to form different isopoly chromates anions.  $\text{CrO}_3$  dissolves in an alkali to give yellow colored  $\text{CrO}_4^{2-}$  ions solution. At very high pH, above 8, the chromate ions,  $\text{CrO}_4^{2-}$ , exist as the discrete entities but as the pH is lowered down, the protonation and dimerization take place. For instance:



The polymeric anions  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{Cr}_3\text{O}_{10}^{2-}$  and  $\text{Cr}_4\text{O}_{13}^{2-}$  produced by the polyacids  $\text{H}_2\text{Cr}_2\text{O}_7$ ,  $\text{H}_2\text{Cr}_3\text{O}_{10}$  and  $\text{H}_2\text{Cr}_4\text{O}_{13}$ , can successfully be isolated from their aqueous as sodium or potassium polysalts like  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{K}_2\text{Cr}_3\text{O}_{10}$  and  $\text{K}_2\text{Cr}_4\text{O}_{13}$ , respectively. Among the isopoly-anions of  $\text{V}^{5+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Mo}^{6+}$  and  $\text{W}^{6+}$ , only  $\text{Cr}^{6+}$  is found to have tetrahedral  $\text{CrO}_4^{2-}$  units joined through the corners. The other metal ions form isopolyanions by the sharing of edges of octahedral  $\text{MO}_6$  units. This may be attributable to the small size of  $\text{Cr}^{6+}$  which can afford only four oxide ions around itself.



The structure of chromate and isopoly anions of chromium.

The tri-chromate and tetra-chromate anions can be crystallized as their alkali metal salts only from strongly acidic solution and no polymerization beyond the tetrameric entity is observed. The Cr–O–Cr bond angle of all polychromates is approximately  $120^\circ$ .

## Isopoly Acids?

Isopoly acids are inorganic acidic compounds that form from the combination of acids or anions of the same type. In this formation process, a water molecule is eliminated during the combination of two acids or anions. Some examples of isopoly acids include isopolychromate, isopolymolybdate, isopolytungstate, isopolyvanadate, isopolyniobates, etc.

For example, isopoly acids of molybdenum forms when molybdenum trioxide is dissolved in aqueous sodium hydroxide. It can form dimolybdate, trimolybdate, tetramolybdate, etc. These acids form from the combination of the basic unit  $\text{MoO}_6$ . Since this basic unit has an octahedral geometry, the isopoly acidic compounds form via the combination of either the corners or edges of these octahedral units. However, this combination that occurs through the corners causes repulsion between the Mo metal atoms. And, this repulsion can be reduced using another metal, other than molybdenum.

## Heteropoly Acids

Heteropoly acids are inorganic acidic compounds which form from the combination of acids or anions of different types. Usually, these acids are combinations of oxygen and hydrogen atoms with particular metals and nonmetals. These acids are very important as re-usable catalysts in chemical reactions. They have applications as both homogeneous and heterogeneous catalysts.

There are a few requirements we have to check before categorizing an acid as a heteropoly acid. It should have a metal (e.g. tungsten, molybdenum, etc), oxygen atom(s), an element from the p-block of the periodic table, and hydrogen atoms that are acidic. The metal atoms are called addenda atoms. There are four types of heteropoly acids.

1. 1:12 tetrahedral
2. 2:18 tetrahedral
3. 1:6 tetrahedral
4. 1:9 tetrahedral

Furthermore, some examples of heteropoly acids include  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{H}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$ , etc.

## Difference Between Isopoly and Heteropoly Acids

A poly acid is an acidic compound which forms from the combination of two acids via elimination of water molecules. The key difference between isopoly and heteropoly acids is that isopoly acids form from the combination of similar acids or anions whereas heteropoly acids form from the combination of different acids or anions. Therefore, isopoly acids have the same repeating unit but heteropoly acids have different repeating units.

Examples of isopoly acids include isopolychromate, isopolymolybdate, isopolytungstate, isopolyvanadate, isopolyniobates, etc. Examples of heteropoly acids include  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{H}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$ , etc.