PERIYAR INSTITUTE OF DISTANCE EDUCATION (PRIDE)

PERIYAR UNIVERSITY

SALEM - 636 011.

B.Sc. CHEMISTRY

FIRST YEAR

PAPER – I : GENERAL CHEMISTRY AND

PRACTICAL – I : INORGANIC ANALYSIS AND PREPARATION

Prepared By :
V.S. GANESWARAN
S.G. Lecturer
Dept. of Chemistry
Arignar Anna Arts College
Namakkal – 637 001.

B.Sc. CHEMISTRY

FIRST YEAR

PAPER – I : GENERAL CHEMISTRY AND

PRACTICAL – I : INORGANIC ANALYSIS AND PREPARATION

INTRODUCTION

In this Paper - I of I B.Sc chemistry we are going to discuss the general chemistry and not a specific branch of chemistry.

That is in general chemistry our discussion will be about the three main branches of chemistry namely In - organic, Organic and Physical chemistries.

In - organic chemistry comprises of two units, Organic chemistry consists of only one unit and Physical chemistry is of two units.

In unit - I of In - organic chemistry Atomic structure is discussed in detail. In unit - II Principles qualitative analysis, is studied giving importance to mainly to Semi micro technique.

In Organic chemistry, that is in unit - III importance is given to structure of bonding, cyclo alkanes and reaction mechanism.

In the first part of unit - IV of physical chemistry, our main topic of discussion is chemical bonding and hydrides. In the second part of unit - V, we will see about the gaseous state, solid state and physical properties and chemical constitution.

B.Sc. CHEMISTRY

FIRST YEAR

PAPER – I : GENERAL CHEMISTRY AND

PRACTICAL – I : INORGANIC ANALYSIS AND PREPARATION

UNIT - I

ATOMIC STRUCTURE

1.1. Fundamental Particles of matter:

Their composition - Comparison between Rurtherford's model of atom and Bohr's model - Outline of the Bohr-sommerfeld model - its limitations - Black body radiation - Photo electric effect - de Broglie theory - Heisenberg's uncertainty principle - Quantum numbers.

Wave mechanical concept of atom - Schrodinger's wave equation (derivation not needed) - Significance of □□and□□□ - Eigen functions and Eigen values - shapes of different orbitals - differences between and orbit and orbital.

1.2. Electronic structure:

Pauli's Exclusion principle and its application - Hund's rule - its basis and applications - stability of half - filled and fully - filled orbitals - Aufbau principles and its limitations.

1.3. Periodic properties:

Atomic and ionic radii, ionisation energy Electron affinity and Electronegativity - Definition , variation of the periodic properties along periods and groups - theoretically explanation for the variations.

1.4. s,p,d and f block elements:

Classification and characteristic properties.

UNIT - II

2.1. Principles of Qualitative analysis:

Basic principles of Inorganic semimicro analysis - semimicro techniques - principles involved in Na_2CO_3 extract preparation - common ion effect and solubility product and their applications in qualitative analysis - separation of cations into groups.

2.2. Principles of volumetric analysis:

Definition of molarity, molality, normality and mole fraction - Definition and examples for Primary and Secondary standards. Theories of acid - base, redox iodo metric and iodi metric titrations - calculations of equivalent weight - Theories of acid - base, redox, adsorption and fluorescence indicators and choice of indicators.

UNIT - III

STRUCTURE AND BONDING

3.1. Electron displacement effects.

3.1.1. Inductive, inductomeric and steric effects - their effects on properties of compounds.

3.1.2. Mesomeric, resonance, hyperconjugation - localised and delocalised chemical bond.

3.2. INTERMOLECULAR INTERACTIONS:

Dipole - dipole interaction, vander Walls forces, hydrogen bond its types - effect of intermolecular forces on physical properties - melting point, boiling point and solubility.

3.3. REACTIVE INTERMEDIATES:

Carbocations, carbanions, free radicals and carbenes with examples.

3.4. CYCLO ALKANES:

Wurtz reaction, Dieckmann ring closure and reduction of aromatic hydrocarbons - Bayer's strain theory and its limitations - Sache - Mohr theory - Ring strain in small rings (cyclopropane and cyclobutane) - theory of strainless rings.

3.5. REACTION MECHANISM:

Methods of determination of reaction mechanism - product analysis, detection of intermediates - Kinetic isotope effects - Primary and Secondary - Kinetic and Stereochemical studies.

3.6. ALKENES:

Electrophilic and free radical mechanism of addition in alkenes - Markownikoff's rule - peroxide effect - mechanism of Hydroboration, Ozonalysis and allylic substitution by NBS - polymerisation.

1,2 and 1,4 additions - thermodynamic and kinetic controlled products - Diels - Alder reaction - synthesis of dienes - 1,3 butadiene, isoprene and chloroprene.

UNIT - IV

4.1. CHEMICAL BOND

4.1.1. Ionic bond - mode of formation - properties of ionic compounds - inert pair effect - Born - Haber cycle - polarisation of ions - factors affecting polarisation - importance of polarisation of ions - Fajan's rules and applications.

4.12. Covalent bond - mode of formation - properties of covalent compounds - valence Bond theory - Postulates of Pauling -

Slater’s theory - Different types of overlapping. Molecular orbital theory - Postulates - Bonding and antibonding molecular orbitals - Tabulation of various M.Os formed from atomic orbitals - Energy level diagrams for M.Os - Bond order - Electronic configuration of Hetero nuclear diatomic molecules - CO, NO and HF.

4.1.3. COORDINATE BOND:

Mode of formation - importance of coordinate bond in the formation of metal complexes.

4.2. HYDRIDES, CARBIDES AND NOBLE GASES

4.2.1. HYDRIDES

Classification- Types of Hydrides and periodic Table - Ionic Hydrides LIH and NaH - Preparation, properties, uses and structure.

Covalent Hydrides - silanes - General study - chemistry of monosilanes and disilanes - Differences between silanes and alkanes.

Metallic Hydrides - Preparation, properties. Structure and uses (a brief study) - Complex Hydrides - $NaBH_4$ and $LIAlH_4$ - preparation, properties, uses and structure.

4.2.2. Carbides - Preparation, properties and technical applications.

4.2.3. Noble gases - position of Noble gases in the periodic table - preparation, properties and structure of compounds of Xenon.

UNIT - V

5.1. THE GASEOUS STATE:

5.1.1 BEHAVIOUR OF IDEAL GASES:

Kinetic molecular theory of gases - the kinetin gas equation - Derivation of the gas laws - Kinetic theory and temperature - Boltzmann constant - Mazwell,s distribution of molecular velocities - types of molecular velocities - collision diameter - collision frequency - mean free path - Degree of freedom of gaseous molecules - Principles of equipartition of energy.

5.1.2. BAHAVIOUR OF REAL GASES:

Deviation from ideal bebaviour - Explanation of deviations -Boyle point. The virial equation of state - derivation of the principles of corresponding states.

5.2. THE LIQUID STATE:

5.2.1. STRUCTURES OF LIQUIDS:

Vapor pressure - Trouton’s rule - surface tension - surface energy - some effects of surface tension - viscosity - effect of temperature on viscosity - (Experimental determination of surface tension and viscosity not necessary) - Refractive index - specific refraction - molar volume and chemical constitution - parachor and chemical constitution - viscosity and chemical constitution - Molar refraction and chemical constitution.

PRACTICAL - I INORGANIC QUALITATIVE PREPARATION AND INORGANIC PREPARATIONS.

1. Inorganic qualitative analysis:

Analysis of a mixture containing two cations and two anions of which, one will be an interfering ion. Semimicro methods using the conventional scheme with hydrogen sulphide may be adopted.

Anions to be studied: Carbonate, sulphide, sulphate, nitrate, fluoride, chloride, bromide, borate, oxalate, arsenite, arsenate, phosphate and chromate.

Cations to be studied: Lead, Bismuth, Copper, Cadmium,

arsenic, Iron,

aluminium, Cobalt, Nickel, Zinc, Barium, Calcium Magnesium and Ammonium.

2. Inorganic preparations.

a. Sodium thiosulphate,

b. Ferrous ammonium sulphate,

c. Tetrammine Copper (II) sulphate and

d. Microcosmic salt.

PAPER - I - INTRODUCTION

This covers both inorganic organic and physical chemistry which comes under Paper - I general chemistry. In this block we will discuss the important basic concepts in various branches of chemistry.

The first two units are assigned for inorganic chemistry.

In the first unit we are going to learn about the structure of atom and the advancements in overcoming the defects of basic atomic models. The latest wave mechanical concept of atomic model including Schrodinger's wave equation is also outlined.

In the second unit our concentration of discussion will be mainly on qualitative and quantitative analysis. In qualitative analysis importance will be given to basic principles. As for as quantitative analysis is concerned the concentration is only on volumetric analysis.

The second unit deals only with organic chemistry.

The third unit is spent for the study of structure and bonding in organic compounds. Here we are around the electron displacement effects, inter molecular interactions reactive intermediates cyclo alkanes and alkenes.

The fourth and fifth unit mainly deals with physical chemistry.

In the fourth unit our point of discussion will be on various types of chemical bonding, M.O theory and M.Os of some diatomic molecules.

In the fifth unit Importance is given to topics like behaviour of ideal gases real gases and liquid state.

In ideal gas discussion will be on kinetic theory of gases, kinetic gas equation, Boltzman constant Maxwell's distribution collision diameter and principle of equipartition energy.

As for as the ideal gases are concerned we are to discuss the deviation from ideal behaviour, Boiling point the virial equation and the principle of corresponding states.

Importance will be given in liquid states to vapour pressure Trouton's rule surface energy viscosity specific and molar refraction Then the study will extend to physical properties and chemical constitution Parachor viscosity and chemical constitution and optical exaltation.

UNIT - I

INTRODUCTION

We give importance to deal with the fundamental particles of matter, various atomic models, growth and development of atomic models and quantum numbers.

Wave mechanical concept of atomic structure, Schrodinger wave equation Eigen functions and the differences between an orbit and orbital are also dealt with here.

Then in the second phase our discussion is mainly on electronic structure of atoms and the periodic properties of elements in general and on the basis of comparative account.

UNIT - I

ATOMIC STRUCTURE

John Dalton in 1809 stated that atom is the hard, dense and smallest indivisible particle of matter. The term atom was derived from the Greek word meaning cannot be cut.

Many theories have been put forward to explain the structure of atom as follows.

DALTON’S ATOMIC THEORY

Dalton in his theory about atom has stated that,

1. All matter is made up of extremely smallest particle called atom.
2. They cannot be further subdivided.
3. They can neither be created nor destroyed.
4. Atoms of the same element are similar to one another in all respects including weight.
5. Atoms of different elements have different properties and different weight.
6. The chemical combination between two or more elements takes place by the union of the atoms of those elements in the simple numerical proportions.

RUTHERFORD’S SCATTERING EXPERIMENT.

Ernest Rutherford allowed a narrow beam of □ - particles to fall on a very thin sheet of Gold or Silver and then allowed the emerging □ - particles to strike a fluorescent screen. On the basis of continuous observations on the above experiments Rutherford found that,

1. Most of the □ - particles pass through the metallic sheet which shows that the atom has more of empty space in it.
2. A small number of □ - particles got deflected to a wider range and even backward also showing the presence of a heavy positively charged body only in a very small volume at the centre of the atom.

RUTHERFORD’S ATOMIC MODEL

Based on his scattering experiments and the discovery of Neutron by Chadwick, Rutherford proposed the following atomic model.

1. An atom is made up of a minute positively charged centre called Nucleus.
2. Though small in size the nucleus contain all the protons and neutrons of an atom.
3. The entire mass of an atom depends only on the mass of protons and neutrons in the nucleus.
4. Since all the atoms are electrically neutral, there must be sufficient number of extremely small negatively charged particles called electrons around the nucleus.
5. In order to overcome the electrostatic force of attraction the electron must be revolving round the nucleus at a very high speed at a longer distance at an order of 10^{-8} cm from the nucleus.

ATOMIC NUMBER

The number of protons (or electrons) in the nucleus of an atom is called its atomic number of the element. Atomic number is represented by Z.

No two elements can have the same atomic number. So atomic number is taken as its fundamental property.

MASS NUMBER

The total number of protons and neutrons present in the nucleus of an atom is called the mass number of that atom. The mass number of an atom (or element) is represented by A.

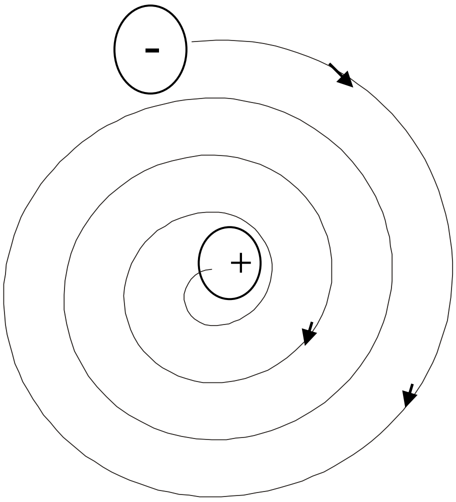
Since the mass of a proton and neutron is approximately equal to 1 atomic mass unit (amu), the atomic mass of an element will be approximately equal to its mass number.

DRAWBACKS OF RUTHERFORD'S MODEL

1. The main drawback lies in its inability to explain the atomic stability. He says that if the electrons are at rest, they will fall in to the nucleus due to the force of attraction by the proton in the nucleus. This will cause the destruction of the atom. That is why he assumes that the electrons are revolving in circular orbits.

But during the revolution of the electron in a circular path, naturally, they will loose energy continuously due to radiation.

As a result the orbit will go on smaller and smaller tracing a spiral path and finally drop in to the nucleus as shown below which will cause destruction of the atom.



But this doesn't happen and all the atoms are extraordinarily stable.

2. The continous emission of energy by electron must give continuous spectrum. But the actual spectrum of Hydrogen is with discrete lines.

Thus the Rutherford's classical model fails to explain the stability of atom and the appearance sharp spectral lines.

BOHR'S ATOMIC MODEL

To overcome the defects in rutherford's model, NeilsBohr with the help of Planck's quantum theory suggested the following theory.

1. The atom consists of a positively charged nucleus with electron revolving around.
2. Electron can move only in certain definite paths called orbits. Electrons in each orbit have a definite energy.
3. An electron can occupy only that orbit in which the angular momentum of the electron is an integral multiple of $h/2\pi$

$$\text{i.e. } mvr = n\frac{h}{2\pi}$$

Where n can be 1, 2, 3, 4, ...

h = Plank's constant

m = mass

v = velocity

r = radius of orbit.

4. Since each orbit is associated with definite energy, they may be called energy levels. The energy levels are characterised by the values of n, and called K, L, M, etc. cells for n = 1, 2, 3 etc. respectively.

5. The energy level nearest to the nucleus is the least energy level and called the ground state. Electron occupying the ground state is the most stable one.

6. An electron can move from one level to another by absorbing or emitting discrete quantity of energy called a quantum of energy.

The quantum of energy absorbed or emitted

i.e. $\Delta E = E_2 - E_1 = h\nu$

7. An electron jumping to higher energy state by absorbing a quantum of energy is said to be in the exited state.

8. The radius of the orbit of H - atom can be calculated using the energy of spectral lines.

LIMITATIONS OF BOHR’S MODEL:

Though Bohr’s model is a very successful one it has the following limitations.

1. It explains the spectrum of atom with one electron systems like H, and He^+ only.
2. It fails to explain the distribution and energy of electron in an atom.
3. It explains the formation of spectral lines but not the formation of fine spectral lines.
4. It is a mixture of quantum and classical theory which are opposite to each other.

That is the frequency of radiation emitted corresponds to quantum theory but the motion of electron in its orbits correspond to classical mechanics.

SUCCESS OF BOHR THEORY :

1. It enables the calculation of energy and radius of orbit in H - atom.
2. Explains the position of various spectral lines of H - atom.

COMPARISON BETWEEN RUTHERFORD AND BOHR MODEL

RUTHERFORD MODEL	BOHR'S MODEL
Electron revolution is in a continuous orbit	Electron revolution is in different orbits
Emission of energy is continuous	Emission of energy is discontinuous
Spectrum obtained will be continuous	Spectral lines will be discrete
Electron looses its total energy and finally dies	Can loss or gain energy only in discrete quantities
As a result atom is unstable	Atom is stable
Radius of orbit in H - can't be calculated.	Radius of orbit in H - can be calculated.

BOHR SOMMERFELD MODEL:

Bohr's model successfully explained the formation of various spectral lines for Hydrogen but failed to explain the spliting of these lines into group of fine lines under high resolution.

To account for this Sommerfeld suggested sub energy levels in each main energy levels.

The sub - energy levels are elliptical in shape. He stated that there will be 'n' different energy levels including the elliptical orbit for a given circular energy level of 'n'.

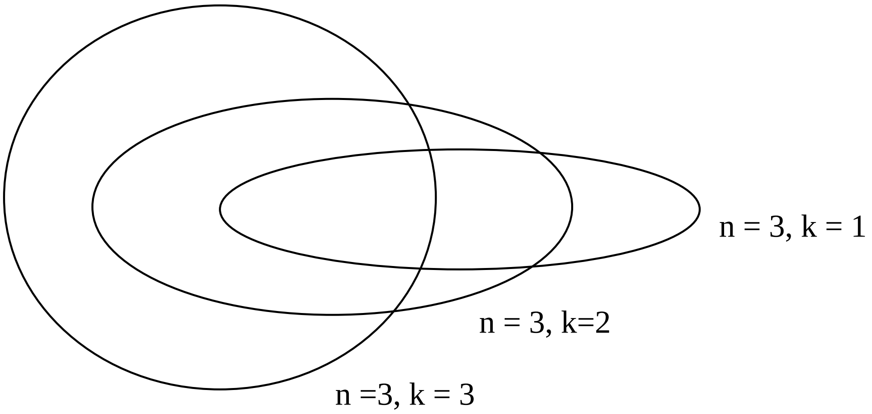
That is, the first circular energy level has no sub elliptical energy level.

But the Bohr's second circular orbit has only one Sommerfeld's elliptical orbit.

For third circular orbit --- 2 elliptical sub-orbits'

for fourth circular orbit---- 3 elliptical sub-orbits and so on.

This concept can be schematically represented as follows.



LIMITATIONS.

According to Sommerfeld, the spectra of the third orbit of H - atom must contain six lines because third orbit will split in to three sub energy levels second to two sub levels and first to one sub level.

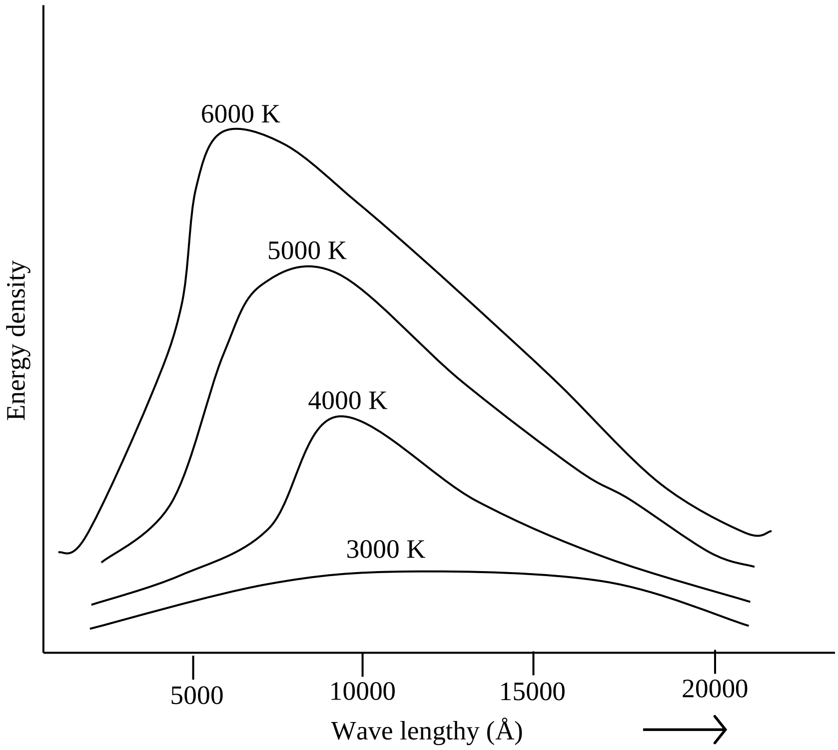
But actually only five lines were observed for the third energy level. Therefore it becomes only a partial fulfillment . Any how the fault is not with the theory but due to the omission or spin factor of electrons.

BLACK BODY RADIATION:

An object that absorbs all the radiations falling on it is known as a black body.

A perfect absorber must also be a perfect emitter of radiation. Thus of all the objects heated to a given temperature a black body radiates the maximum energy.

The amount of energy radiated per unit area called the energy density by a black boy depends on its temperature. However the energy radiated at a particular temperature will not be of single frequency. The correlation between the energy density and wave length at different temperature is as represented below.



These curves shows that,

1. At each temperature the wave length of maximum energy radiated various.
2. As the temperature increases the position of the maximum shifts towards the lower wave length.
3. The higher the temperature the higher the maximum.

The energy distribution in black body radiation cannot be explained by classical theory. So Max Planck discovered a mechanism for black body radiation on the basis of quantum theory.

QUANTUM THEORY OF RADIATION:

According to MaxPlanck's quantum theory or radiation,

1. Radiant energy emitted or absorbed is discontinuous in the form of tiny quantities called quanta.
2. Each quantum is associated with definite amount of energy depending upon the frequency of radiation.

I e.. $E = h\nu$

where E = energy in joules

□□□□□□□□□□□□□□ = frequency

h = Plank’s constant = 6.626*10$^{-34\ \mathrm{Js}}$

3. A black body can emit or absorb energy only in whole number multiples of quantum namely □h□, 2h□,3h□, ...nh□.

Fractional absorption or emission of energy is not possible. This phenomenon is called the quantisation of energy.

PHOTOELECTRIC EFFECT:

Sir J.J.Thomson found that *when a light of certain frequency falls on the surface of some metal plate in vacuum electrons are ejected from that metal plate. This phenomenon is known as Photo electric effect.*

Few metals like Cesium which has lower ionisation energy shows this effect even in visible region. On the other hand many more metals show this effect only with the high energy uv - light.

After having a careful study, Thomson observed that,

1. For each metal certain minimum frequency of incident light is essential to eject the electron. This minimum frequency is called the threshold frequency represented by □$_0$.
2. The threshold frequency is different for different elements.
3. The kinetic energy of the ejected electron is independent of the intensity of incident light, but is directly proportional to the frequency of incident light.
4. Number of ejected electrons is directly proportional to the intensity of the incident light. That is the number of photo - electrons emitted is directly proportional to the number of photons striking the metal plate.

The photo electric effect is well explained by the particle theory, but the wave theory doesn’t.

EXPLANATION ON THE BASIS OF QUANTUM THEORY:

Quantum theory considers light as bundles of energy which are called the photons.

The energy of each photon is considered to be equal to be equal to h□ where h is the Planck’s constant and □ is the frequency of light.

The threshold energy of a photon is sufficient to release the electron by breaking its binding energy.

When a photon of certain energy strikes a metal surface some of its energy is consumed to detach the electron from the metal and the remaining energy will be carried by the ejected electron.

Example:

Calculate the (i) the energy of the photon in eV (ii) the kinetic energy of the emitted photo electron and the velocity of photo electron when a photon of wave length 4000A^{o} strikes a metal surface, the work function or the metal being 2.13eV and the mass of the electron is = 9.109 X10^{-31}kg.

Solution:

(i). Energy of photo electron:

Frequency of light $\upsilon = c\lambda$

c = velocity of light = $3\times10^{8}\,ms^{-1}$

λ = wavelength of light = $4000\times10^{-8}\,m$

$$\frac{c}{\lambda} = \frac{4000\times10^{-10}}{3\times10^{8}}$$

But $1.602\times10^{-19}\,J = 1eV$

$$\text{Energy E} \quad h\upsilon = 6.626\times10^{-34}\times\frac{4000\times10^{-10}}{3\times10^{8}} = 3.10eV$$

Energy $= 3.10$ eV

de - BROGLIE THEORY :

de - Broglie stated that similar to light, matter particles can also behave like waves under proper condition.

On this basis He derived an expression for the wave length of the wave associated with any particle, similar to that of a proton. He used mass energy relationship as follow

Energy of a moving particles given by $E = mc^{2} \quad \rightarrow (1)$

where E = energy of the particle wave

m = mass the particle and

v = velocity

The energy of the associated wave $E = h\upsilon \quad \rightarrow (2)$

where h = Planck's constant and

□ = is the frequency of light.

From 1 and 2 we get,

$$h\upsilon = mc^2$$

$$\text{Since } \upsilon = \frac{c}{\lambda}$$

$$mc^2 = h\frac{c}{\lambda}$$

$$\text{i.e. } \lambda = \frac{hc}{mc^2}$$

$$= \frac{h}{\rho} \quad (mc = \rho = \text{momentum})$$

This relationship is called *de* - Broglie relationship and the wavelength calculated using this relationship is called the *de* - Broglie wave length.

EXAMPLE :

Calculate the *de* - Broglie wave length of an electron moving with a velocity of 1.20 X 10^5 m s^{-1}. Mass of the electron is 9 X 10^{-31} kg.

h = 6.629 X 10^{-34}.

SOLUTION ;

We know that □ = h/mc

$$\lambda = {}^{h}\!/_{mc}$$

$$\lambda = \frac{6.626\times10^{-34}}{9.1\times10^{-31}\times1.20\times10^{5}}$$

$$\therefore \text{ the de}-\text{Brogile wave length } \lambda = 6.08\times10^{-9}\text{m} = 60.60\text{A}^0$$

HEISENBERG'S UNCERTAINTY PRINCIPLE :

The principle states that, *it is impossible to determine precisely both the position and the momentum (velocity) of a small moving particle simultaneously.*

Mathematically it is represented as follows.

$$\Delta x \times \Delta h \approx {}^{h}\!/_{4\pi}$$

Where □ x is the uncertainty in position and□□□□□□□□□□□□□□□□□□□

□□□□□□□□□□□□□□□□□□□□□□□□□p is the momentum.

Evidently if □ x is very small i.e. the position is known more of less exactly, then □p will□be very large and vice versa.

Therefore it is possible only to predict the probability of locating an electron with a particular energy.

EXAMPLE :

An attempt was made in locating an electron in an atom within a distance of 0.1 A^{o} . Calculate the uncertainty involved in the measurement of its velocity.

Mass of electron = $9.1 \text{ X } 10^{-31}$ kg.

Planck’s constant = $6.626 \text{ X } 10^{-34}$ Js·

SOLUTION

We know that,

$$\Delta x \times \Delta h \approx {}^{h}\!\diagup_{4\pi}$$

$$\text{or } \Delta x \times m\Delta v = {}^{h}\!\diagup_{4\pi}$$

$$\text{i.e } 0.1 \times 10^{-10} \times 9.1 \times 10^{-31} \times \Delta v = 6.626 \times 10^{-34}$$

$$\therefore \quad \Delta v = \frac{6.626 \times 10^{-34}}{0.1 \times 10^{-10} \times 9.1 \times 4\pi}$$

$$= 7.3 \times 10^{7} \text{m}$$

QUANTUM NUMBERS :

In an attempt to find a solution to the complexity in spectra, quantum numbers were introduced. Quantum numbers are the numbers which explain the various energy levels of an electron.

Out of four quantum numbers introduced the three quantum numbers namely n, l and m are defined by wave mechanical treatment of H - atoms.

The can be explained as follows.

PRINCIPAL QUANTUM NUMBER :

The principle quantum number of an electron is represented by ‘n. It decides to a larger extent, the main energy of an electron. It also determines the average distance of a an electron from the nucleus. The energy levels are visualised as shells or circular orbits.

‘n’ can have any value from 1. That is n can be 1, 2, 3, 4, ---------etc. As the value of n increases the energy of the electron and its distance from the nucleus increases.

If n = 1 then the energy level is K shell

n = 2 then the energy level is L shell

n = 3 then the energy level is M shell

n = 4 then the energy level is N shell and so on.

ANGULAR MOMENTUM QUANTUM NUMBER:

It was assumed that a portion of the total energy must be associated with the orbital motion of the electron around the nucleus. The angular momentum due to orbital motion of the electron is represented by angular momentum quantum number or azimuthal quantum number or subsidiary quantum number.

Azimuthal quantum number is represented by ‘l’ and l can have n values from 0 to (n-1).

That is for n = 1; l can be 0 only

for n = 2; l can be 0 and 1.

for n = 3; l can be 0, 1 and 2 and so on.

The values of l gives the nature of sub energy levels where the electron is located. The angular momentum quantum numbers are represented by the letters s, p, d, f and so on. These letters are derived from the old spectral terms namely sharp, principal, diffused and fundamental. It gives the angular momentum and shapes of the electron levels whether circular or elliptical.

If l = 0 it represents s - orbital,

l = 1 it represents p - orbital,

l = 2 it represents d - orbital,

l = 3 it represents f - orbital and so on.

MAGNETIC QUANTUM NUMBER :

The angular momentum of the electron will produce a magnetic field. This magnetic field interacts with the external electrical or magnetic field. Due to this interaction the electrons in a given energy sub - level orient themselves in certain specific region of space around the nucleus. These regions of space are called orbits.

This number of orientations of orbitals in a given main energy level is given by magnetic quantum number.

It is represented m and it can have 2l+1 values form -l through 0 to +l.

For n = 1

l = 0 (n values)

m = 0 only (2l+1 = 1 value only)

For n = 2

l = 0 and 1 (n values that is 2 values)

For l = 0 m can be 0 only

l = 1 m can be (2l+1 = 3 values) -1, 0 and +1.

SPIN QUANTUM NUMBER :

The spin quantum number was not derived from wave mechanical treatment. It was found that the electron possessed intrinsic angular momentum or spin. That is the spin quantum number represents the spin or rotation of the electron about its own axis.

It is represented by s it can have a value of +1 or -1.

WAVE MECHANICAL OR QUANTUM MECHANICAL CONCEPT OF ATOM

THE POSTULATES OF WAVE MECHANICS:

The Newton’s theory of classical mechanics well explains the behaviour of macro particles like a planet, a cricket ball etc. But it fails to explain completely the behaviour of sub - atomic particles like an electron.

Hence in order to define the behaviour of sub - atomic particles a new theory called wave theory was developed and its postulates are

1. The electron is no longer a point mass moving in an orbit but instead a standing wave.
2. The physical state of a system at time ‘t’ is described by the wave function (x, t).
3. The wave function (x, t) its first and second order derivatives are continuous, finite and single valued for all values of x.

With these basic postulates Schrodinger derived an equation for the associated waves as follows,

THE SCHRODINGER WAVE EQUATION :

With the evidences that the electron has dual character Erwin Schrodinger derived an equation for waves. That is the discrete energy levels proposed for electrons by Bohr was replaced by a mathematical function .

the wave function is related to the probability of finding an electron at various places (orbitals) around the nucleus.

After doing so many manipulations, Schrodinger gave the following equation for an electron wave propagating.

The Schrodinger is,

$$\frac{\delta^2\psi}{\delta x^2}+\frac{\delta^2\psi}{\delta y^2}+\frac{\delta^2\psi}{\delta z^2}+\frac{8\pi^2 m\left(E-V\right)}{h^2\psi}=0$$

Where is the wave function,

x, y and z are three space co - ordinates,

m is the mass of the electron and

V is the potential energy associated with the electron.

Here □□ is directional proportional to the probability of finding an electron in space.

SIGNIFICANCE OF □ and □□ .

The wave function □ itself has no significance because it gives only the amplitude of the electron wave.

How ever the square of the wave function namely □□ has very important significance because it gives the probability of finding an electron of the given energy in an orbital around the nucleus.

EIGEN FUNCTIONS And EIGEN VALUES :

An acceptable solution of Schrodinger wave equation is called the Eigen function.

Schrodinger wave equation can have several solutions. But not all of them are acceptable. So, that function , which is an acceptable one is called the Eigen function.

The acceptable wave function or the Eigen function must satisfy the following conditions.

1. The function should be finite . That is for each values of the variables x, y, and z there must be only one value for □.
2. It must be single valued.
3. It should be continuous. That is there must not be any sudden change in the value of □, when the variables are changed.

The schrodinger equation yields significant solutions for certain definite values of the total energy E. These values are called the Eigen values.

An Eigen value equation is as follows.

$$H\square_n = E_n\square_n \quad (n = 0, 1, 2, 3 \text{--------})$$

Where n is the quantum number,

H is the Hamiltonian factor

$\square_n$ is the Eigen functions,

E_n is the Eigenvalues.

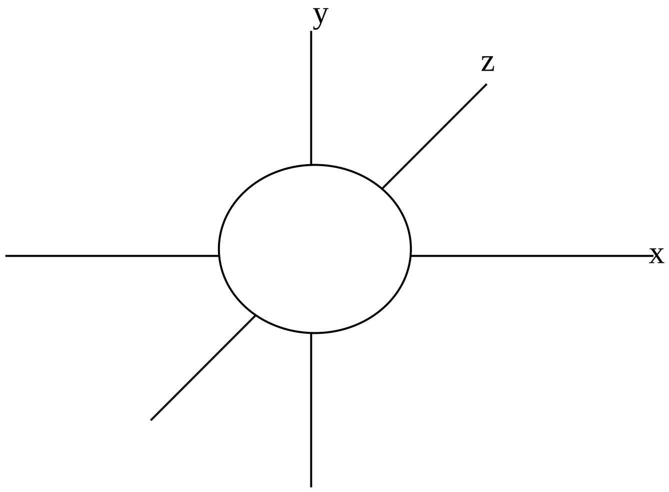
SHAPES OF ORBITALS ;

An orbital represents a definite region in three dimensional space around the nucleus of an atom where the probability of finding an electron with specific energy os the most.

The shapes of orbitals depend on the azimuthal quantum number ‘l’ and not on ‘n’.

Shape of ‘s’ orbital.

If the azimuthal quantum number is ‘0’ then we get ‘s’ orbital. Since ‘m’ has only one value namely ‘0’ the s orbital has only one orientation. It is symmetrical over all the directions and spherical in shape. The electron density of the s - orbital is uniformly distributed around the nucleus and very close to the nucleus as depicted below.

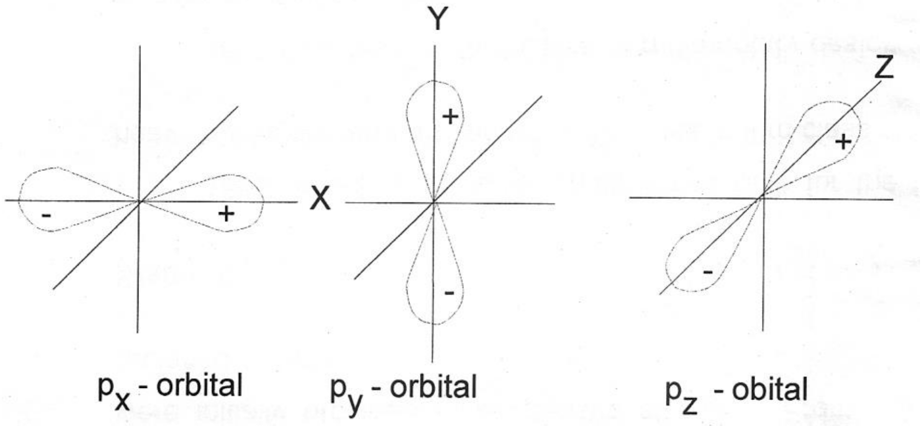


s orbital

Shapes p - orbitals:

If the value ‘l’ is equal to 1 we get the p - orbitals. The p - orbitals are dumbbell shaped. Since for ‘l’ = 1, ‘m’ has three values namely -1, 0 and +1 the p - orbitals have three different orientations though they are same in size.

The three different orientations are towards the three co - ordinates namely the x, y, and z axes. The density of the electrons at the nucleus is zero. Electron density of p - orbitals becomes more and more as the distance of the orbital from the nucleus increases. We can show the shapes of different p - orbitals as follows.



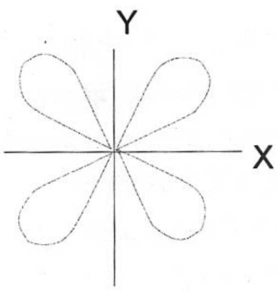
The + and the - signs are only the geometric signs and should not be confused with the +ve and -ve charges.

Normally all orbitals with ‘l’ = 0 have zero electron density at the nucleus. That is the probability finding these electrons at the nucleus is zero.

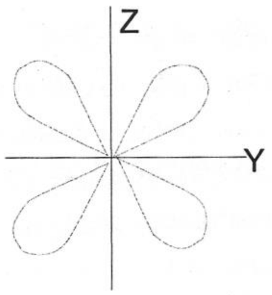
Shape of ‘d’ orbitals :

For the value of ‘l’ = 2 we get d - orbitals. Since for ‘l’ = 2 we get five values for ‘m’ namely -2, -1, 0, +1 and +2 d- orbitals have five different orientations.

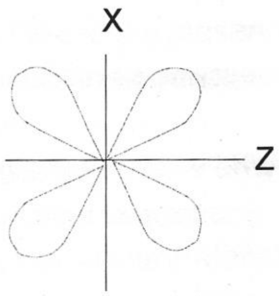
The five d = orbitals are d_{xy}, d_{yz}, d_{zx}, $d_{x2 - y2}$ and d_{z2}. The d_{xy}, d_{yz} and d_{zx} orbitals are same in shape but differ in orientation. The remaining two orbitals differ both in shape and orientation as shown below.



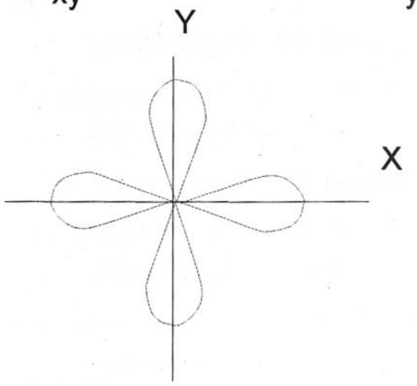
d_{xy}

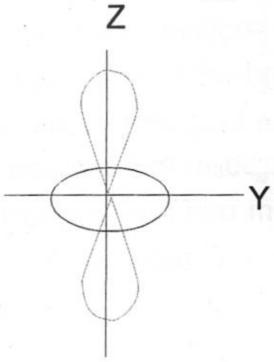


d_{yz}



d_{zx}





As usual the electron density of d - orbitals at the nucleus is zero since ‘l’ = 0.

Differences between an orbit and an orbitals.

Orbit	Orbital
1. It is the circular or elliptical path traced by an electron at a fixed distance from the nucleus.	It is the region in space around the nucleus where the probability of finding the electron is maximum.
2. The maximum number of electrons in an orbit is $2n^2$ where ‘n’ represents the orbit’s number.	The maximum number of electrons in orbital is 2 only.
3. Orbits are associated with fixed energy.	The energy of an orbital corresponding to a region in space can be calculated by solving wave equation.
4. Orbits don’t have any directional character.	All orbitals except s - orbital have directional characters.
5. This concept is against the Heisenberg’s uncertainty	This concept is in accordance with the Heisenberg’s

principle.	uncertainty principle.
6. It doesn’t agree with the	It agree with the wave character.

ELECTRONIC STRUCTURE :

PAUL’S EXCLUSION PRINCIPLE AND ITS APPLICATIONS :

Pauli’s exclusion principle states that no two electrons in an atom can have the four quantum numbers the same. Therefore in an atom any two electrons can have three quantum numbers same but the fourth one namely the spin quantum number must be different.

Example:

For K shell ‘n’ = 1 and

‘l’ = 0 for both the electrons.

But ‘s’ must be +1 for one electron

and -1 for the other electron.

Applications:

1. This principle is very much useful in determining the maximum number of electrons that can be present in any energy level as illustrated below.

For ‘L’ shell,

‘n’ = 2	‘l’ = 0	‘m’ = 0	‘s’ = +1	s orbital
			= -1	
	‘l’ = 1	‘m’ = -1	‘s’ =+1	p_X orbital
			= -1	
		‘m’ = 0	‘s’ = +1	p_Y orbital
			‘s’ = -1	
		‘m’ = +1	‘s’ = +1	p_Z orbital
			‘s’ = -1	

Thus it is clear that K shell can have 2 electrons, L shell can have 8 electrons, M shell can have 18 electrons and so on.

In general an energy shell can have $2n^2$ electrons where ‘n’ is the principle quantum number.

HUND’S RULE :

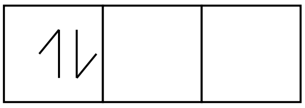
According to Pauling’s exclusion principle, all the four quantum numbers of any two electrons in an atom can’t be same. Hence each orbital can accommodate two electrons but with opposite spins.

But in the case of degenerate orbitals, that is orbitals with same energy like p_x, p_y and p_z if two electrons with opposite spin are placed in the same orbital then the electrostatic repulsion will be greater than that when they are placed in separate orbitals.

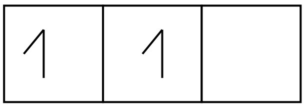
Therefore to have least repulsion, electrons should be placed singly in degenerate orbitals until a condition arises.

This fact forms the basis of Hund’s rule which states that “ *electron pairing in any orbital is not possible until all the available orbitals of a given set contain one electron each* “. This rule is also called the Hund’s rule of maximum multiplicity.

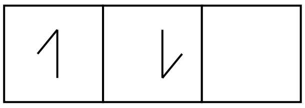
To prove this fact let us consider the following three arrangements of two electrons in the p - orbitals.



(1)



(2)



(3)

In (1) Two electrons though with opposite spins are placed in the same sub-shell. So the repulsion energy. So the repulsion energy will h be maximum.

But in (2) and (3) the two electrons are placed in different sub orbitals. Hence the repulsion in these two arrangements must be low as compared to the (1).

In (2) both the electrons are placed with same spin where as in (3) they are placed with opposite spins. In (2) the electrons can exchange their orbital easily with one another since they have same spin. During this process of exchange energy of the system decreases consequently increasing the stability of the system.

This type of electron pairs are called the exchange pairs and the energy lost during the exchange is called the exchange energy. It is denoted by - E.

But in the arrangement (3) the two electrons are with opposite spin and hence there can’t be any exchange possible. Even there is an exchange the energy of the system will increase since we have to add energy in order to unpair the spin of the electrons. As a result the energy of the system increases consequently decreasing its stability.

Therefore out (2) and (3) arrangements, (2) is the most stable one in accordance with the Hund’s rule of maximum multiplicity.

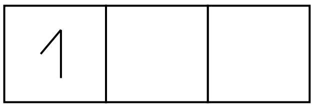
APPLICATIONS :

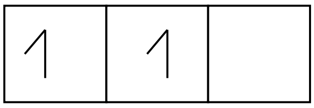
Stability of half filled and completely filled orbitals.

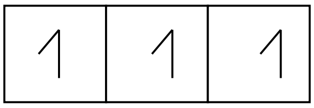
When we place two electrons in the same orbit with opposite spin we have to spend energy. This energy required to place two electrons together in the same orbital is called the pairing energy denoted by P. Pairing energy increases the energy of the system as a whole thus decreasing its stability.

Therefore the overall stability of the system is controlled by the exchange energy (E) and the pairing energy (P).

With these background let us consider the following three electronic arrangements.


(1)


(2)

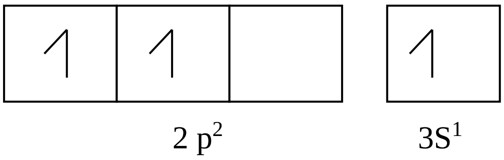

(3)

In the arrangements (1) there can’t be any exchange and so there is no any exchange energy gained.

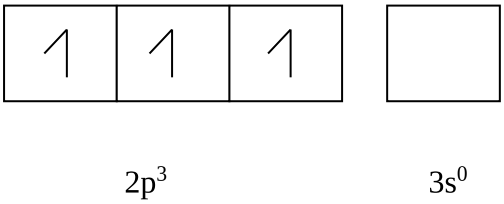
In (2) there is a possibility of one exchange and hence there will be one exchange energy.

But on the other hand in (3) there are three exchanges and there must be three exchange energies possible and comparatively the arrangement (3) is the most stable.

Let us consider the fallowing two arrangements namely (4) and (5).



(4)

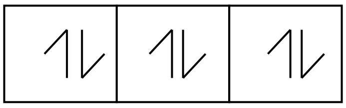


(5)

In the arrangement (4) there is one exchange in the p - orbital and no exchange is possible in the s - orbital. There fore there is a gain of one exchange energy only. On the other hand in the arrangement (5) there are three exchanges possible in the p - orbital resulting three exchange energies.

Consequently the completely half filled configuration (5) is the most stable one.

Let us consider the following completely filled configuration.



(6)

In the completely filled arrangement (6), there are six exchange energies and three pairing energies. But pairing energies are high when compared to the exchange energy. Hence the completely filled arrangement must be less stable. On the other hand this arrangement is highly stable. This property is attributed to the symmetry of electron distribution. That is in a completely filled and completely half filled arrangements there is a balance or uniform density of electron cloud around the nucleus, where as there is no balance of electron cloud in an incompletely filled arrangement.

This accounts for the extra stability of half filled and completely filled electronic arrangements.

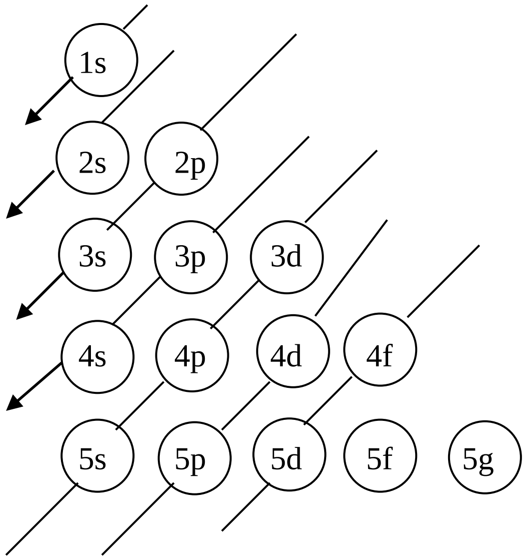
AUFBAU PRINCIPLE (or) BUILDING UP PRINCIPLE :

Aufbau is derived from the German word meaning ‘building up’. This principle states that “*the orbital with lower energy is filled first before an orbital with higher energy state is filled”.*

In other words the electrons enter the orbitals in the increasing order of energy. The orbitals in the increasing order is as follows.

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, etc.

A handy method to write this order can be shown as follows.



That is a new electron enters an orbital where (n+l) is minimum. If the (n+l) value is the same for two or more orbitals then the electron enters the orbital where ‘n’ is minimum.

For example let us consider 3d and 4p orbitals. The (n+l) value for both the orbitals is (3+2) and (4+1) respectively which equals 5. But the 3d orbital is filled first because it has lower value of ‘n’.

Examples.

Electronic configuration of

$$Na = z = 11 = 1s^2 2s^2 2p^6 3s^1$$
$$Cl = z = 17 = 1s^2 2s^2 2p^6 3s^2 3p^5$$

Limitations of Aufbau principle.

1. This principle gives the way of filling electrons in main shells but doesn’t give the details of distribution in sub - orbitals. For example Nitrogen has $1s^2 2s^2 2p^3$ configuration. In the p - orbital electrons may have paired arrangement or unpaired arrangement. This problem is not solved by aufbau principle. Hund’s rule of maximum multiplicity gives solution to this problem.
2. Chromium with atomic number 24 and Copper with atomic number 29 must have the following electron arrangements.

$$Cr = 1s^2 2s^2 2p^3 3s^2 3p^6 4s^2 3d^4$$
$$Cu = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$$

But actually they have the following arrangements.

$$Cr = 1s^2 2s^2 2p^3 3s^2 3p^6 4s^1 3d^5$$

$$Cu = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$$

It is because completely half filled orbitals more stable than partially filled orbitals.

3. According to this principle 4f must be filled first prior to 5d. But in actual practice 5d is filled prior to 4f orbitals. This is because the energy difference between the two are very minimum.

PERIODIC PROPERTIES :

The characteristics exhibited by atoms are called the atomic properties. The recurrence of similar atomic properties of elements after certain regular interval, when they are arranged in the increasing order of atomic number is called the periodicity of properties. This led to the conclusion that periodicity in propertied of elements can be explained in the basis of their electronic structure. Elements having similar electronic configuration were found to have similar properties.

Various atomic properties of elements can be explained in detail as follows.

Atomic radii :

The distance between the centre of the nucleus and the outer most shell of electrons in an atom is called its atomic radius.

There is a periodic variation of atomic radius with atomic number. Generally when we move from the left to right in a period the atomic radius goes on decreasing Where as in a group the atomic radius go on increasing when we move from the top to bottom.

This can be explained as follows. In a period for example in the second one when we go from Li to F atomic number goes on increasing by one unit. But the electron increment is made to the same shell. As a result of this the attractive force between the electrons and the protons in the nucleus increases. As a result of this the atomic radius goes on decreasing.

On the other hand when we move along a group for example in first group atomic number goes on increasing but the incoming electrons go to the higher shell. Hence naturally the size the atom goes on increasing.

Drawbacks.

But the atomic radii are not as precise as we explained earlier. Since according to wave mechanics it is difficult to fix the exact position of a moving electron. More over the atoms are not in a completely isolated state.

These facts made difficulties in giving the exact atomic radius. Hence to overcome this, three operational concepts of atomic radius namely i) co - valent radii, ii) van der waal's radii and iii) ionic radii were introduced. Out of these we will discuss about the ionic radii in detail as follows.

Ionic radii.

Ionic radius is the distance from the centre of the nucleus of an ion to the edge of its electron cloud.

A cation is formed by the loss of one or more electrons from an atom. This generally results in the removal of the outer most shell as a whole. There fore the size of the +ve ion is very much reduced. More over as the number of electrons decreases, the effective nuclear charge increases and so the attractive force between the electrons and the nucleus increases very much and this effect also reduces the size of an ion. These effects tend to reduce the cationic size.

Thus the ionic radius of any cation is less than the atomic radius of the corresponding atom. When we move down a group there is an increase of ionic radii.

As for as the anions are considered (-ve ion) they are formed by the addition of one or more electrons to outermost shell of that particular atom. As a result of this the effective nuclear charge decreases resulting in the expansion of the electron cloud. Consequently the radius of the -ve ions namely anions increases. In moving from left to right in a period the anionic radii also goes on increasing progressively.

Ionisation energy (or) Ionisation potential, I.E.

The energy required to remove an electron from an isolated gaseous atom of that element to a +ve ion is called its ionisation energy or ionisation potential. It is represented by the symbol I E.

$$M(g) + E \longrightarrow M(g) + e^-$$

The energy required to remove the first electron to form M+ ion is called the first ionisation energy. Successive ionisation energies are called the second, third and so on ionisation energies.

But usually the ionisation energy of an atom means the first ionisation energy only.

Variation in the periodic table.

In a group.

When we pass from the top to the bottom of a group the ionisation energy goes on decreasing. This fact is attribute to the following facts.

1. Though the nuclear charge increases as we pass down the size of the atom gradually increases which decreases the electrostatic force of attraction between the nucleus and the electrons in the outermost orbitals.

2. Screening effect.- Since there is an increase in the number of inner electrons and consequently the increase in the number of inner shells, there is a screening between the nucleus and the outermost electrons. As a result of this the electrostatic force of attraction decreases making the outermost electrons loosely bound.

These two effects make the ionisation potential to decrease when we move down in a group.

The over all increase in the nuclear charge is less effective when compared to the screening effect.

In a period.

When we move from the left to right in a period the ionisation energy goes on increasing. This fact can be explained as follows.

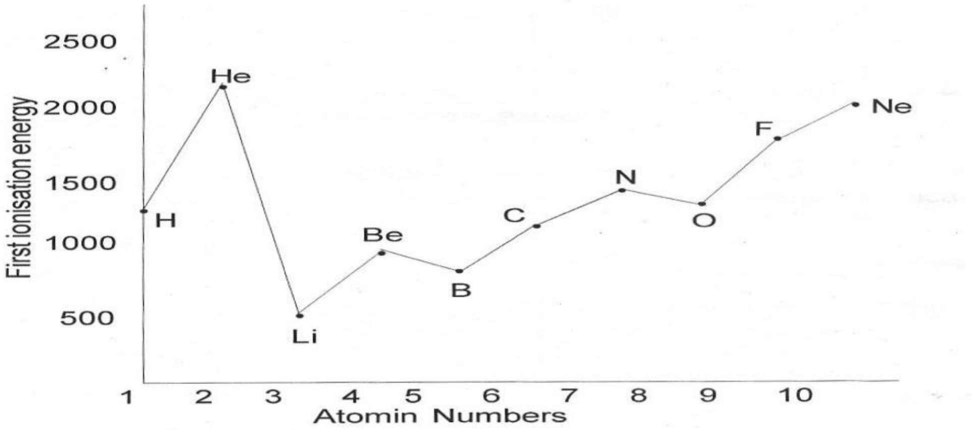
1. The nuclear charge goes on increasing and hence the electrostatic force of attraction goes on increasing.

2. There is gradual decrease of atomic size which decreases the atomic radius thus by increasing the electrostatic force of attraction. This produces an increasing difficulty to remove an electron.

As a result the ionisation energy goes on increasing when we pass from the left to the right in a period.

But the variation in a period is not as smooth as that in a group. That is there is some irregularities in the ionisation energy along the period.

For example let us take the ionisation energies of the second period as depicted below.



This shows that, the atomic size alone is not a criteria to decide ionisation energy. Apart from that the stability of the atom also plays an important role.

From the above diagram it is clear that ionisation energy of Boran and Oxygen are unexpectedly low when compared to their preceding Beriliyam and Nitrogen respectively. This fact can be explained by the consideration of the electronic configuration of these elements which are as follows.

Be = $1s^2$, $2s^2$

B = $1s^2$, $2s^2$, $2p^1$

N = $1s^2$, $2s^2$, $3p^3$

O = $1s^2$, $2s^2$, $2p^4$

In Berilyam both the orbitals have completely filled configuration and hence becomes more stable, making it difficult to the remove the electron.

In Boron in the 2p orbital there is a single electron. Therefore it is less stable arrangement and so it becomes easy to the remove the outer most electron.

In Nitrogen the 2p orbital is half filled. Therefore it has extra stability which makes it difficult to remove its electron.

But in Oxygen there is no symmetry in electron arrangement of 2p orbital and hence the stability is not as great as in Nitrogen. So its ionisation is energy is lesser than that of Nitrogen.

On the other hand in Neon it has completely filled and an octet arrangement which makes it very high stable. So it has the highest ionisation energy.

In Lithium the incomplete 2s1 arrangement makes less stable and hence with lesser ionisation energy.

Factors determining ionisation energy.

1. Atomic size.

The larger the atomic size the lesser the ionisation energy. It is because in larger atoms the distance between the nucleus and the outer most electron orbit is larger. There fore the electrostatic force of attraction is less, making it easy to remove an electron. But in smaller atoms due to the smaller distance the force of attraction will be higher and so the ionisation energy will be high.

2. Nuclear charge.

Force of electrostatic attraction increases with the increase in nuclear charge. There fore the increase in the nuclear charge results in the increase of ionisation energy of an element.

3. Screening effect.

As the number of electrons in an atom increases, the number of inner shells also increase. The inner shells shield the outer most electrons from the nucleus. This effect, reduces the electrostatic force of attraction between the nucleus and the outer shell electrons. This effect is called the screening effect which makes easy for the outer electron to be removed.

4. Penetrating effect.

Among the s, p, d and f orbitals the s orbital is very close to the nucleus. That is the s electrons penetrate more towards the nucleus. Hence it is more attracted by the nucleus when compared to the p, d and f orbital electrons which are far away from the nucleus. There fore it becomes very difficult to remove s electrons when compared to the others. Thus the ionisation energy of various orbit decreases in the order s>p>d>f.

5. Electronic configuration.

We know that the half filled and the completely filled electron arrangements are more stable than any other arrangements. There fore these stable electronic configuration has more ionisation energy when compared to the other configurations.

ELECTRON AFFINITY or AFFINITY ENERGY :

Electron affinity of an atom is the tightness with which it binds an additional electron.

Electron affinity is the energy released when an electron is added to a gaseous isolated atom. The chemical reaction can be written as follows.

$$X (g) + e^- \longrightarrow X^- + \text{Energy.}$$

Electron affinity, also called affinity energy is represented by EA. The greater the energy released in taking up an electron by an atom, the greater is its electron affinity.

Variation in the periodic table :

When we move from the top to bottom of a group the electron affinity goes on decreasing.

It is because as we move down in a group the size of the atom increases and so the distance of the outer electrons from the nucleus goes on increasing. But we know that the greater the distance the lesser is the electrostatic force of attraction. So bigger atoms loosely bind the additional electrons and hence the electron affinity decreases as the size increases.

On the other hand along a period electron affinity increases when we move from the left to right. It is because as the atomic number goes on increasing along a period the size of the atom are going decreasing. This increases the force of attraction and there fore smaller atoms have more affinity towards additional electrons. As a result in a period the electron affinity goes on increasing as the atomic number increases.

Thus it is clear that the electron affinity of Metals is low as compared to that of non metals.

It was observed that halogens have the maximum electron affinity. It is because the less stable s^2p^5 configuration of halogens attains the more stable s^2p^6 when they acquire additional electrons.

But in the case of Fluorine the electron affinity is abnormally low even though it has very small size. It is because the smaller size of Fluorine finds it difficult to accommodate an extra electron due to congestion and more electrostatic repulsion.

Successive electron affinities .

Like ionisation energies successive electron affinities are also possible but very low because after getting an electron the become -vely charged ions and so repels the second and third electrons.

Factors affecting electron affinity :

1. Atomic size.

Smaller the size, the greater the affinity towards the electron and hence smaller atoms have higher electron affinity. But since bigger atoms have lesser affinity towards electron due to the decreased electrostatic force of attraction, they have lesser electron affinity.

2. Nuclear charge.

As the nuclear charge increases, that is as the number of protons in the nucleus increases the attractive force also increases resulting in higher electron affinity.

3. Electronic configuration :

As we know that since the half filled and the completely filled orbitals have extra stability than the other elements they are not ready to accommodate any additional electrons. Therefore elements having the above electronic configuration have lesser electron affinity.

ELECTRO NEGATIVITY :

Different investigators have defined the electronegativity in different ways. But Pauling defined electronegativity as *the tendency of an atom in a molecule to attract electrons to itself.*

It can be illustrated by taking the molecules Cl_2 and HCl which have the following structures.

$$\mathrm{Cl} \overline{\qquad\qquad} \mathrm{Cl} \qquad\qquad \overset{\delta^+}{\mathrm{H}} \longrightarrow \overset{\delta^-}{\mathrm{Cl}}$$

In chlorine molecule the bond is shared by two chlorine atoms which will have similar electron attracting capacity. So the bonded electron will not move to any side making both the atoms neutral. There fore there will be no net gain or loss of electron and hence bond is a pure co valent bond.

On the other hand in HCl molecule the bonded electron is shared between two different electrons. So in the competition to pull the bonded electrons chlorine having more electron attracting power it pulls the electron more towards it self thus getting more electron density and making the H - atom partially +ve as shown in the above diagram. This type of bonds are called the polar co valent bonds. Normally a polar co valent bond is more stable than a normal co valent bond.

This shows that in HCl molecule chlorine is more electronegative than H - atom.

It is very difficult to measure the electro negativity vales. Though it is assumed to be a constant for a particular atom it is not constant. It is dependent on the environment.

Pauling, Mullikan and Alfred Rochow have calculate the its value by their own methods. But now a days we are following the electro negativity values of Pauling’s. The latest calculated values of electronegativities of certain elements can be tabulated as follows.

Element :	= H	Li	Be	B	C	N	O	F
Electro negativity	= 2.2	1.0	1.5	2.0	2.5	3.1	3.5	4.1

in Pauling’s scale

Variation in the periodic table :

In a period when we move from the left to right the size of the atom is going on increasing and so the electro negativity also is going on increasing.

In a group when we move from the top to bottom we know that the size of the atom goes on increasing and hence the electro negativity goes on decreasing.

FACTORS AFFECTING ELECTRO NEGATIVITY :

1. Size of the atom.

The size of the atom very much decides the electro negativity of elements. The smaller the atom the greater the electrostatic force of attraction and hence the larger the electro negativity of the atom.

2. Shielding effect.

As the number of electrons in an atom increases the number of inner shells also increases making a screening between the nucleus and the outer most shell. As a result the atom looses its capacity to attract any extra electrons resulting in decrease of electro negativity.

3. Electron affinity and Ionisation potential.

The electro negativity depends on the ionisation potential and electron affinity values. If the ionisation potential is high then it becomes very difficult to remove a electron. In other wards that atom has a tendency to attract the extra electron. Similarly if the ionisation potential of an atom is more then it is clear that, that atom will attract electron easily. Therefore if the ionisation potential and the electron affinity of an atom is high then its electro negativity must also be high, except Fluorine whose electronegativity is the highest even though its electron affinity is very low.

4. Electronic configuration.

Atoms with nearly filled configuration are eager to have an electron because the attain stability by doing so . There fore such atoms also have more electro negativity.

5. Oxidation state of the atom.

For example let us consider the three oxidation states of Iron namely Fe, Fe+ and Fe2+. Since the +ve charge of any atom increases naturally its size must decrease and the effective nuclear charge must increase. These two factors altogether increases the electro negativity of that species.

6. Effect of substituents (or) Effect of environment.

Electro negativity of an atom also depends on the substituent attached to it. For example let us take CF_3I and CH_3I. The carbon atom in CF_3I has more +ve charge than that in the CH_3I molecule. Hence it is clear that the carbon atom of the former molecule is more electronegative.

7. Hybridisation.

We know that out sp, sp2 and sp3 hybridised orbitals the sp orbital has more s - character which implies that the sp - orbitals more penetrating to the nucleus than the other two. Therefore sp - electrons will be closer to the nucleus and hence the sp - hybridised carbon must have more electronegativity.

s, p, d AND f BLOCK ELEMENTS :

CLASSIFICATION :

The elements arranged in the long form of the peiodic table can be divided in to four main blocks namely s, p, d and f block elements. This classification is based on the type of the orbitals to which the last electron of the atom of an element enters. They can be discussed in detail as follows.

s- Block elements.

The elements having ns^1 and ns^2 configurations are called the s - block elements. The group - I alkali metals and group - II alkaline earth metals come under this block.

p - Block elements.

Elements with ns2 np1--6 configuration are called the p - block elements. That is the successive electrons enter in to the p - orbital of the elements in this block.

The s- and the p- block elements are called the representative elements.

d - Block elements.

Elements having (n-1)d^{1--10} ns^{1--2} electronic configuration are classified in to d - block. In these block of elements the successive electrons enter in to the penultimate (n-1)d orbital and hence they are called the transition elements.

f - Block elements.

The elements in which the electrons inter the f - orbital are called f-block elements. Here the electrons enter in to ante penultimate shell namely the (n - 2)f shell. Therefore they are called the inner transition elements.

CHARACTERISTICS OF :

s - Block elements.

1. Physical properties.
    a. All are silvery white, soft and light metals. Their melting points are low. Atomic volume is also high.
2. density.
3. Since their atomic volumes are high consequently their density is low.
4. Since the solitary 1s1electron is loosely bound to the nucleus their ionisation energy is very low. That is the outer most electron can be easily removed.
5. They have very high electro +ve character. So they have very low electronegativity.
6. They all are univalent in nature and easily form M+ ions.
7. Since they loose easily electrons they have a very good reducing property.
8. As a result of their high electro positivity the easily form ionic bonds with halogens.

But as the group - II alkaline earth metals are considered they are moderately hard in nature. So they have higher melting point.

They have more density than the corresponding alkali metals.

These are electro positive and are bi valent in nature.

Alkaline earth metals are strong reducing agents.

Both the alkali metals and the alkaline earth metals show flame colouration.

Since 2s2 electrons easily overlap with np orbital these elements are very good conductor of heat and electricity.

p - Block elements.

Their properties mainly depend on the p electrons. p - block elements have metallic, non - metallic and metalloid characteristics. They give mostly co - valent compounds.

Generally they have higher ionisation potentials and higher electronegativity values.

Except Fluorine most of them exist as +ve and -ve ions.

p - Block elements have a special property called inert pair effect. That is electrons of p - orbitals alone get in to chemical reactions where as the s-electrons are not.

d - Block elements.

All of them of metals.

The atomic size of d block elements are less than that of s- block elements but more than p- block elements.

All of them have variable valencies.

Their metallic compounds act as catalyst.

Most of them give coloured ions in compounds or in solutions.

The properties of p - block elements lie in between the more metallic s - block elements and more non - metallic p - block elements and hence these are called the transition elements.

f - Block elements.

Lanthanide and Actinides come under the f - block elements. They are also called rare earth elements.

In lanthanides prime oxidation number is +3. Oxidation states +2 and +4 also exist.

Since successive electrons enter in to the antepenultimate shell there is contraction in the size of the Lanthanides. This property is called the lanthanide contraction.

As the actinides are concerned they exist in +2, +3, +4, +5, and +6 oxidation states. But the +4 state is the commonly found one.

Similar to Lanthanides Actinide contractions is also noticed.

EXPECTED QUESTIONS :

1. Calculate the values of various quantum numbers for the principle quantum number n = 1.
2. Calculate the maximum number of electrons that can be accommodated in the M shell.
3. Using the aufbau principle write the electronic configurations for atoms with atomic numbers 54 and 95
4. Give the differences between the orbit and the orbital.
5. What is periodicity?. Give any two periodic properties .
6. Define Hund's rule of maximum multiplicity.
7. Why the d- block elements are called the transition elements?.
8. Discuss the atomic properties of s- block elements.
9. Why the electron affinity of Fluorine is low where as the electronegativity is high?.
10. Write note on screening effect.

Problems.

1. Calculate the wave length associated with the electron of mass $9.1X10^{-31}$ kg moving with an energy of $5.76X10^{-15}$J

(h = $6.626X10^{-34}$ Js

2. The velocity of electron in the first orbit is 10^{6} m s^{-1} · Supposing that the electron can be located in the orbit within 0.1 A^{o} calculate the uncertainty in the velocity.

NOTES

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

…………………………………………………………………………………...

UNIT – II

INTRODDUCTION

Unit -II deals with the basic principles of semi micro technique in inorganic salt analysis which is an economic and latest sophisticated technique.

Here we deal with the important principles like solubility product and separation of cations into various groups.

Then in the second half of the unit quantitative analysis that to mainly volumetric analysis is given importance.

In this section molarity, molality and normality of solutions details primary and secondary standards theories of acid - base titrations calculation of equivalent weight - are dealt with in detail.

UNIT -- II

PRINCIPLES OF QUALITATIVE ANALYSIS:

INTRODUCTION :

Qualitative and quantitative analysis come under the branch of Analytical chemistry. But qualitative analysis forms the basis of analytical chemistry.

Qualitative analysis plays a vital role in the following fields as details below.

Agriculture - soil analysis

Geology - rocks and mineral analysis

Medicine - poison in tissue analysis for the purpose of

diagnosis and criminology

Qualitative analysis is defined as " *the finding out of or identifying the constituents present in an unknown substance* ". It needs qualities of patience and careful manipulation.

There are three methods of qualitative analysis used in inorganic chemistry. They are,

1. MACRO METHOD :

In macro method, samples of a fraction to a few grams, solution of large volumes ranging from 10 to 100 ml and ordinary test tubes beakers and funnels are used.

2. MICRO METHOD :

Analysis of very small quantity of samples with a drop to a few of solutions using diminutive apparatus and special instruments such as microscope is called the macro technique.

3. SEMIMICRO METHOD :

Analysis of samples of 0.05 -- 0.1 mg with solutions of few drops to 2 ml using small test tubes called semimicro test tubes, centrifuge tubes, semimicro suction funnels heating block etc. are called the semi micro technique.

Semi micro technique is very close to micro methods rather than to macro.

This method uses the same scheme of reactions as in ordinary qualitative analysis but with modified techniques.

SEMI MICRO TECHNIQUE :

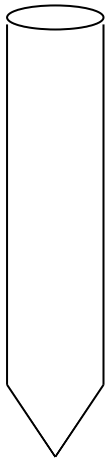
1. Centrifugation :

Filtration can be done by three methods namely by decantation, filtration and by centrifugation.

If the whole of the precipitate is in the form of large dense crystals then any of these three methods can be used. But decantation is the least satisfactory method and filtration is a time consuming one.

But the centrifuge used in semi micro technique is a high speed rotating machine operated mechanically or electrically. During centrifugation the centrifugal force realised by the particles of the precipitate in centrifuge tube makes the precipitate to settle very quickly and completely at the bottom.

Out of all these three methods centrifugation is the fast and best method. The centrifuge tube can be depicted as follows.



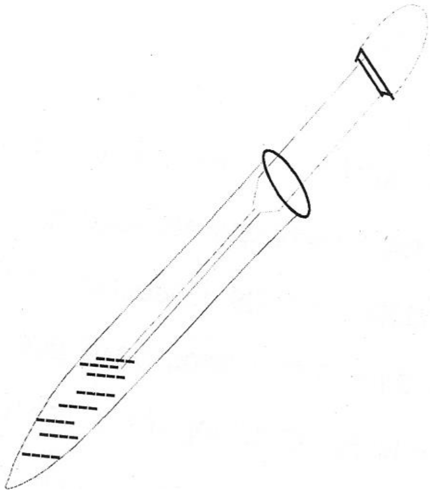
WASHING :

The precipitate must be washed to remove any unwanted ions adhering to the precipitate otherwise it will interfere with the regular analysis. The regular method of washing and discarding the washings will be a tedious proces. But using centrifugation the washings can be easily done any number of times as we need which save the time spent for settling of the precipitate.

DCCANTATION;

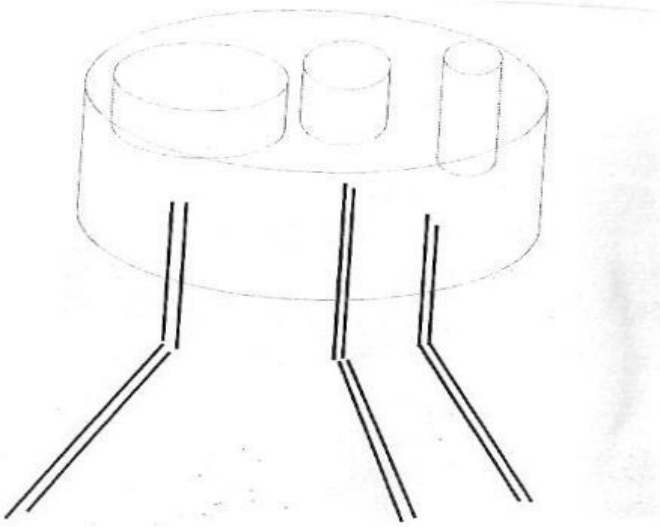
During washing the precipitate each time the washings or supernatent liquid can be discarded by filterration or by decantation.

But in the semimicro method dropper pipettes are used to remove the washing in a sophisticated way. The set up used can be shown as follows.



HEATING BLOCK :

It will be inconvenient to heat a small semi micro test tube or a beaker in a free flame. So an Aluminium heating block as shown below is used for heating purposes more conveniently.



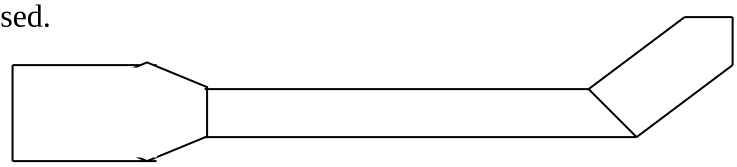
Cylindrical cavities are made in the block to place the apparatus to be heated. Using this heating block we can heat a semi micro test tube boiling tube and a beaker at a time. Thus this method of heating saves our time, fuel and also more safety.

SPOT TESTS :

Glazed porcelain plates with several small cavities is called the spot - reaction plate is used for spot tests. These tests are very much useful for conducting confirmatory tests involving colour reactions and colour precipitates.

NICKEL SPATULA :

In addition to glass stirrer a Nickel spatula of small size as shown below is used.



PRINCIPLES INVOLVED IN SODIUM CARBONATE EXTRACT :

Only few anions like nitrate, chloride, sulphate etc. form water soluble salts. But most of the anion like phosphate, borate, fluoride etc. form water soluble salts only with alkali metals like sodium and Potassium.

Therefore to get the anions into solution for precipitation reactions they have to be converted in to Sodium salt by double decomposition. Sodium carbonate is found to be the best suited for this purpose.

This double decomposition reaction taking place in this process can be explained by taking Barium phosphate as the example.

$$Ba_3(PO_4)_2 + 3Na_2CO_3 \longrightarrow 2Na_3PO_4 + 3BaCO_3$$

In this reaction the phosphate takes the soluble form and the calcium ion is converted in to an insoluble carbonate.

The filtrate obtained after a strong heating of the insoluble salt with sodium carbonate and sufficient quantity of water is called the “sodium carbonate extract”.

PREPARATION OF SODIUM CARBONATE EXTRACT :

About 50 mg of the insoluble salt say Barium phosphate mixed with about 150 mg of Sodium carbonate is taken in a semi micro beaker along with 5 ml of distilled water. Then the contents of the beaker are strongly heated with the help of the heating block for about 10 -- 15 minutes. Then allow the precipitate to settle and after having cooled centrifuge to remove the unwanted and suspended matter.

Then discard the precipitate and preserve the supernatant liquid which is the Sodium carbonate extract.

The extract is alkaline in nature due to the excess use of Sodium carbonate. Therefore before testing for the presence of various anions the excess carbonate must be removed. Otherwise the carbonate will interfere in regular analysis misleading to wrong inferences. To neutralise the extract suitable acid is used and then boiled to expel the dissolved carbon dioxide evolved during neutralisation.

Application:

All the acid radicals can be identified by using the Sodium carbonate extract by adapting suitable procedures. For example halides, nitrate, sulphate, phosphate, oxalate, fluoride, arsenite and arsenate can be conveniently identified using Sodium carbonate extract.

COMMON ION EFFECT :

Definition :

The suppression of dissociation of a weak acid or a weak base by adding a solution of strong electrolyte, having an ion common with the weak acid or weak base is called the common ion effect.

As a result of this phenomenon the concentration of the uncommon ion of the weak acid or weak base is diminished.

Illustration.

Let us consider the dissociation of acetic acid a weak acid as given below.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Suppose that we are adding a strong electrolyte HCl or CH_3COONa to Acetic acid, having H^+ and CH_3COO^- respectively as the common ion.

If we add HCl, the H^+ ion released from HCl which is common, suppresses the dissociation of CH_3COOH by favoring reverse reaction. As a result the concentration of CH_3COO^- decreases.

If we add CH_3COONa the CH_3COO^- ion released from Acetic acid, suppresses the dissociation forward reaction. This results in the decrease of H^+ ion concentration.

As for as H_2S solution is concerned it dissociates as follows

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

If an acid is added to this solution, H^+ ion ionised from the acid will suppress the dissociation of H_2S and hence the sulphide ion concentrations decreases. This effect plays a vital role in the separation of cations in to various group.

Applications.

1. In precipitation reactions of cations by H2S, the concentration of S2- plays the key role. That is if S^{2-} ion concentration is low, only the cations like Copper, Cadmium, Bismuth Arsenic etc. get precipitated. On the other hand if the concentration S^{2-} is larger then cations like Zinc, Cobalt etc. are precipitated. Here in order to decrease the S^{2-} ion concentration HCl is added.
2. Similarly in the precipitation of Aluminium the concentration of hydroxide ion must be low. In order to lower the concentration of hydroxide ion from Ammonium hydroxide Ammonium chloride is added which has NH_4^+ as the common ion.

If the concentration of hydroxide ion in higher then Barium and calcium will also get precipitated.

3. The solubility of a precipitate decreases in presence of a common ion in excess. For example the solubility of AgCl decreases if the concentration of chloride ion is present in excess. Thus common ion effect also plays an important role in the precipitation reactions also.

SOLUBILITY :

Solubility is defined as "*the maximum amount of a solute dissolved in a fixed quantity of a solvent say 100 gm*".

SOLUBILITY PRODUCT :

"*Solubility product* K_S *of a sparingly soluble salt at a particular temperature is defined as the product of the concentrations of ions in its saturated solution*".

Explanation :

Let us take the solution of AgCl, a sparingly soluble salt in water. Ag^+ and Cl^- ions will pass in to solution till a saturated solution of AgCl is formed.

Now an equilibrium will be set between AgCl and its ions as follows.

$$\underset{\text{solid}}{AgCl} \rightleftharpoons \underset{\text{solution}}{Ag^+ + Cl^-}$$

According to the law of chemical equilibrium, the equilibrium constant k ,

$$K_s = \frac{a_{Ag^+} \times a_{Cl^-}}{a_{AgCl}}$$

Since the activity of a solid is unity the equation becomes,

$$K = a_{Ag^+} X a_{Cl^-}$$

Where Ks is the solubility product of AgCl. It is a constant for a particular solvent at a particular temperature.

Application :

1. The principle of solubility product imposes an important condition for the precipitation of substance. That is, only when the ionic product of the substance in solution exceeds the value of K_S , the precipitation is possible.
2. Classification of metallic ions in to various groups in qualitative analysis is based on the solubility products of their chlorides, sulphides, hydroxides and carbonates.

The common cations are classified in to six groups namely group I, II, III, IV, V and VI as follows.

The solubility products of the cations like Pb^{2+}, Ag^{2+} and Hg^{2+} are very low when compared to that of other common cations which are very high. Therefore by adding HCl to the original solution the above ions are precipitated as their chlorides. Thus the cations Pb^{2+}, Ag^{2+} and Hg^{2+} are group I.

When the concentration of the sulphide ion is around 10^{-23} moles per liter the metals like Lead, Mercury, Copper, Cadmium, Bismuth, Arsenic, Antimony and Tin gets precipitated which has very low solubility product where as the cations like Zn^{2+}, Mn^{2+}, Ni^{2+} and Co^{2+} are not precipitated which has high value of K_S.

Therefore the cations Cu^{2+}, Cd^{2+}, Bi^{2+}, AS^{3+}, Sb^{3+} and Sn^{3+} are placed in group II.

But in ammoniacal medium where p^H is equal to 10 the concentration of sulphide ions raise to approximately 10^{-3} moles per liter. At this condition the sulphides of the cations $Zn^{2+,}$ $Mn^{2+,}$ Ni^{2+} and Co^{2+}, which has fairly high solubility product get precipitated. Thus they are placed in group IV.

In a similar when the concentration of hydroxide ions are fairly low the cations like Al^{3+}, Fe^{2+} and Fe^{3+} which has low solubility product get precipitated where as the cations Ba^{2+}, Ca^{2+}, Sr^{2+} and Mg^{2+} are not precipitated which has fairly high solubility products. Hence the cations namely Al^{3+}, Fe^{2+} and Fe^{3+} are placed in group III.

When the concentration of the carbonate ions is fairly low, only the metal ions Ba^{2+}, Ca^{2+}, Sr^{2+} are precipitated as their carbonates. But Mg^{2+} whose carbonate has high solubility product is not precipitated. As a result the cations Ba^{2+}, Ca^{2+}, Sr^{2+} are placed in 5th group.

In order to maintain the concentration of hydroxide ions ammonium chloride is added which has the NH_4^+ as the common ion.

Finally Mg^{2+}, which has high solubility product of its chloride, sulphide, hydroxide, and carbonate, is placed in the 6th group.

Ammonium radical, whose chloride, sulphide, hydroxide and carbonate are highly water solubl, is not placed in any group and tested for its presence separately.

Group reagent :

The precipitant used to precipitate the cations of a particular group is called the group reagent.

For example HCl is the group reagent for the I group, H_2S is the group reagent for the II group and so on.

Advantages of semi micro technique :

1. Saving of time and chemicals.
2. Separation is sharp and quick.
3. Breakage is low.
4. Less noisy.
5. Much space is saved due to smaller reagent shelves and work table.

PRINCIPLES OF VOLUMETRIC ANALYSIS

INTRODUCTION:

There are two methods of qualitative analysis namely gravimetric and volumetric analysis.

Gravimetric analysis involves the measurement of weights where as volumetric analysis involves the measurement of volumes of reagents of known concentration required for complete reaction.

This is also called titrimetric methods and it is one of the most widely used technique of chemical analysis.

PRINCIPLE OF VOLUMETRIC ANALYSIS :

In this technique a known volume of a solution of unknown concentration called analyte is reacted completely with a measurable quantity of an appropriate reagent of known concentration called *titrant.*

The principle of volumetric analysis states that " *equal volumes of equinormal solutions react with each other completely* ".

Mathematically this principle can be given as,

$$V_1 \text{ X } N_1 = V_2 \text{ X } N_2$$

Where V_1 = volume of the titrant,

N_1 = normality of the titrant,

V_2 = volume of the analyte and

N_2 = normality of the analyte.

Thus it is clear that in volumetric analysis, the concentration and volumes of the solutions forms the basic measurements.

The volume is always measured in ml only and the concentration is expressed by molarity, molality, normality and mole fraction. They can be explained one by one as follows.

MOLARITY :

Before going in to the details of molarity it is essential to define number of moles which form the basis of various concentration terms.

The number of moles of a solute is defined as the number gram molecular weight of that solute.

Mathematically number of moles of any solute,

$$= \frac{\text{actual weight of the solute taken}}{\text{Molecular weight of the solute}}$$

For example the molecular weight of Sodium carbonate is found to 56 . Therefore number of moles in 56 gm of Sodium carbonate

$$= \frac{\text{Weight of Sodium carbonate}}{\text{Molecular weight of Sodium carbonate}}$$

$$= \frac{56}{56} = 1$$

Their fore the number of moles = 1.

MOLARITY :

The molarity of a solution is defined as the number of moles of any solute dissolved in 1 liter of the solution.

It is represented by the symbol 'M' and mathematically given

by $= = \frac{\text{number of moles of solute molecules}}{\text{volume of the solution in litre}}$

Example.

Suppose that 392 gms of Mohr's salt is dissolved in one liter of the solution.

$$\text{the number of moles of Mohr's salt} = \frac{\text{Weight of mohr's salt}}{\text{molecular weight}}$$

$$= \frac{392}{392} = 1$$

$$\text{Molarity} = \frac{1}{1} = 1$$

$$M = 1$$

Worked example.

Calculate the molarity of 62 gm of Sodium thiosulphate dissolved in 250 ml of water.

Solution.

Weight of thio dissolved in 250 ml = 62 gm.

Molecular weight of thio = 248.

The number of moles of thio $= \frac{62}{248}$

= 0.25

$$\text{Molarity} = \frac{\text{number of moles}}{\text{volume in litre}}$$

$$= \frac{.25}{250} \times 1000$$

$$= 1.0$$

$$\text{i.e Molarity M} = 1.0$$

MOLALITY :

Molality of a solution is defined as the *number of moles dissolved in 1 Kg of the solvent .*

Molality is represented by ‘m’ and mathematically given as

$$m = \frac{\text{number moles of the solute}}{\text{weight in Kg of the solvent}}$$

Example.

Suppose that 98 gm of Sulphuric acid is dissolved in 1000 ml of the solution say water.

Now number of moles of Sulphuric acid $= \frac{98}{98} = 1$

(Since molecular weight of sulphuric acid = 98)

molality of the solution $= \frac{1}{1} = 1$

NORMALITY :

Normality of a solution is defined the number chemical equivalents dissolved in one liter of the solution .

It is represented by ‘N’ and mathematically given as

$$N = \frac{\text{weight per liter of the solution}}{\text{equivalent weight of the solute}}$$

Equivalent wight.

The chemical equivalence or the gram equivalent weight of a substance is defined as *that weight of it which will combine with or release 1.008 parts by weight of Hydrogen of 8.0 parts by weight of Oxygen or 35.46 parts by weight of chlorine.*

The molecular weight and the equivalent weight of a solute need not be the same.

Example.

Let us say that 4 gm of Sodium hydroxide is dissolved in 500 ml of water. The normality of this solution is calculated as follows.

Amount of Sodium hydroxide dissolved in 500 ml = 4 gm.

Amount dissolved in 1000 ml = 4X2 = 8 gm

Equivalent weight of NaOH = 40

$$\text{Normality } N = \frac{\text{weight per liter}}{\text{equivalent weight}}$$

$$= \frac{8}{40} = 0.2\,N$$

Normality of this NaOH solution = 0.2N

For a long time in volumetric analysis normality was in use to represent the concentration of titrating solutions. But now a days the use of normality scale is almost not in use and only molarity is used in volumetric analysis.

MOLE FRACTION :

Mole fraction of constituent is its fraction per one mole of the total of all the constituents present in the mixture.

It is obtained by dividing the number of moles of the constituent in the solution by the total number of moles of all the constituents in the solution.

Mole fraction is represented by ‘x’ and mathematically it is given as

$$x_A = \frac{n_A}{n_A + n_B}$$

Where x_A = mole fraction of the constituent A

n_A = number of moles of constituent A

n_B = number of moles of constituent B

Example.

Let us consider a solution of 2 moles of alcohol in 3 moles water.

The mole fraction ofalcohol in this solution $= \frac{2}{2+3} = 0.4$

N.B

It is obvious that the sum of mole fractions of all the constituents present in a mixture must be equal to 1.

STANDARD SOLUTION :

In volumetric analysis, solutions of known concentration are used to know the concentration of unknown solutions by titration.

This solution whose concentration is precisely known is called the standard solution. The standard solution is or two types namely

1. Primary standard solution and
2. Secondary standard solution.

PRIMARY STANDARD SOLUTION ;

A primary standard solution is one whose concentration can be known directly from the weight of the solute and the volume of the solution.

A substance used as a primary standard must fulfill the following requirements.

1. They must be available in 100% pure and dry form.
2. Must be stable to atmosphere both in pure and in solution form.
3. Easily available at modest rate.
4. Should be reasonably soluble in the solvent of titration medium preferably in water.
5. Its reaction with an unknown must be stoichiometric and instantaneous.
6. Must have a larger equivalent weight so that the error of normality associated with weighing will be low.

Examples of substances that may be used as primary standards are Sodium carbonate, Oxalic acid, Arsenious oxide, Potassium dichromate etc.

SECONDARY STANDARD SOLUTION ;

A secondary standard solution is one whose concentration can not be directly known from the weight of the solute and the volume of the solution.

A secondary standard solution may be used for standardisation after the standardisation of this solution itself with the help of a primary standard solution.

Examples of substances that can be used for preparing secondary standard solutions are Potassium permanganate, Sodium hydroxide Ferrous sulphate, Iodine solution etc.

PRESERVATION OF STANDARD SOLUTIONS :

Certain precautions should be taken in storing and preserving the standard solution. They are,

1. Bottles or standard flasks must be kept tightly closed to avoid evaporation of solvent from the solution
2. It must be protected from atmospheric gases.
3. The standard solution once with drawn must never be returned to the source.
4. Light sensitive solutions must be preserved in dark coloured containers.
5. Solutions which are affected by bacteria may be protected by adding little of Sodium carbonate.

THEORIES OF TITRATIONS:

Introduction.

Based on the nature of reactions involved titrations are divided in to the following four types.

1. Acid - Base titrations,
2. Oxidation - Reduction titrations,
3. Iodometric titrations and
4. Iodimetric titrations.

The principles in these titrations can be seen one by one.

PRINCIPLE INVOLVED IN ACID - BASE TITRATIONS :

An acid - base titration is further divided into two types as follows.

a). Acidimetric titration.

The titration of a free base or those obtained from salts of weak acid by hydrolysis, with a standard acid is called acidimetry.

e.g.. The titration of NaOH with HCl.

b). Alkalimetry

The titration of a free acid or those obtained by hydrolysis of salts of weak bases, with a standard base is called the alkalimetry.

It is clear that the term acidimetry and alkalimetry just depends on the standard solution used and there is no any other difference.

Both of these titrations in general acid - base titrations the principle is the combination of H^+ and OH^- alone takes place as shown below.

$$H^+ + OH^- \longrightarrow H_2O$$

Since the above reaction is a neutralisation reaction this titration is also called the neutralisation titrations.

Examples

HCl Vs NaOH

HCl Vs NA_2CO_3

$H_2C_2O_4$ Vs NaOH.

OXIDATION - REDUCTION TITRATIONS :

Oxidation is a process in which one or more electrons are removed and reduction is a process in which one or more electrons are added.

Thus in a oxidation - reduction titrations the change of oxidation number or transfer of electrons among the reacting substances take place. Here oxidation and reduction takes place simultaneously and hence this titration is also called the redox titration.

The mostly oxidising agents used are Potassium permanganate, Potassium dichromate.

e.g..

In the titration of $KMnO_4$ with $FeSO_4$ in presence of dilute Sulphuric acid the reactions taking place can be given as follows.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5(O)$$

$$2FeSO_4 + H_2SO_4 + (O) \longrightarrow Fe_2(SO_4)_3 + H_2O$$

In this redox reaction Mn^{2+} is reduced to Mn^{+} and Fe^{2+} is oxidised to Fe^{3+}.

IODO METRIC TITRATIONS :

The titration of iodine liberated in a chemical reaction is called the Iodometric titrations.

e.g.

For example let us consider the titration of $CuSO_4$ with hypo in presence of acetic acid. In this titration, $CuSO_4$ liberates Iodine when KI is added as shown below.

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

Then the Iodine liberated reacts with hypo as shown below to give Sodium tetrathionate and NaI as shown below

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

e.g. (2)

$$K2Cr2O7 + 4H2SO4 \longrightarrow K2SO4 + Cr2(SO4)3 + 4H2O + 3(O)$$

$$6KI + 3H_2O + (O) \longrightarrow 6KOH + 3 I_2$$

IODIMETRIC TITRATIONS :

Iodimetric titrations are the titrations in which Iodine is directly titrated with suitable reagents.

e.g (1).

For example we can have the titration of Iodine directly with Sodium thiosulphate.

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2Nal$$

e.g.(2)

$$Na_3AsO_3 + I_2 + H_2O \longrightarrow Na_3AsO_4 + 2HI$$

The second titration is the titration of Arsenious oxide and Iodine.

CALCULATION OF EQUIVALENT WEIGHTS :

The equivalent mass of any substance is that mass of it which is chemically equivalent to one gram atom of Hydrogen or 1/2 gram atom of Oxygen or one gram atom of Chlorine.

The relation between molecular mass and equivalent mass is given by the equation, equivalent mass $= \frac{\text{molecular mass}}{n}$

Where n corresponds to

1 gram atom of Hydrogen or

1/2 gram atom of Oxygen or

1 gram atom of chlorine.

Using this relationship we can calculate the equivalent mass of various types of compounds as detailed below.

(or)

The equivalent mass of any substance is that mass of it which will combine with or liberate 1 parts by weight of Hydrogen or 8 parts by weight of Oxygen or 35.46 parts by weight of chlorine.

We can illustrate the calculation of equivalent mass of various substances as follows.

EQUIVALENT MASS OF AN ACID :

Let us take HCl for example to calculate the equivalent mass.

Hydrochloric acid dissociates as follows.

$$HCl \longrightarrow H^+ + Cl^-$$

That is it has only one replacable Hydrogen atom.

Therefore the value of n = 1

$$\text{equivalent mass} = \frac{\text{molecular mass of HCl}}{n}$$

$$= \frac{36.45}{1}$$

The equivalent mass of HCl = 36.45.

EQUIVALENT MASS OF A BASE :

For example let us calculate the equivalent mass NaOH.

Sodium hydroxide reacts with an acid as per the following equation.

$$NaOH + H^{+} + Cl^{-} \longrightarrow NaCl + H_2O$$

Thus Sodium hydroxide reacts with one equivalent of H^{+}. Therefore the value of ‘n’ = 1

Hence equivalent mass NaOH = $= \frac{\text{molecular mass of NaOH}}{1}$

Equivalent mass of NaOH = $= \frac{40}{1}$ = 40

EQUIVALENT MASS OF ACIDIC OR BASIC SALTS :

Let us consider the calculation of the equivalent mass of Sodium carbonate. It reacts with an acid according to the following stoichiometry.

$$NaOH + H^{+} + Cl^{-} \longrightarrow NaCl + H_2O$$

Thus in this reaction Sodium carbonate reacts with 2 equivalents of Hydrogen . Hence the value of ‘n’ = 2.

Therefore the equivalent mass of Na_2CO_3 = $= \frac{106}{2} = 53$

EQUIVALENT MASS OF OXIDISING AGENT :

Let us take for example $KMnO_4$ which reacts liberates nascent Oxygen in presence of dilute acid as shown below

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5(O)$$

In this reaction, $KMnO_4$ releases 10 parts by weight of Oxygen.

From this reaction it is clear that,

$2KMnO_4$ 10 (O)

i.e. $KMnO_4$ 5 (O)

Therefore the value of ‘n’ = 5

Thus the equivalent mass of $KMnO_4$ = $= \frac{158}{5} = 31.6$

EQUIVALENT MASS OF A REDUCING AGENT :

Let us take the reactions of Ferrous sulphate with nascent Oxygen in presence of dilute Sulphuric acid as detailed below.

$$2FeSO_4 + H_2SO_4 + (O) \longrightarrow Fe_2(SO_4)_3 + H_2O$$

From this reaction we have,

$2FeSO_4$ 2(O)

i.e. $FeSO_4$ (O)

Thus the value of ‘n’ = 1

There fore the equivalent mass of

$$FeSO4.7H2O \ = \frac{278}{1} = 278$$

FOR SUBSTANCES REACTING WITH CHLORINE :

The reaction of Silver nitrate with Chlorine can be written as follows.

$$AgNO_3 + KCl \longrightarrow AgCl + KNO_3$$

From the above reaction we see that ,

$$1AgNO_3 \equiv 1Cl$$

There fore the value of ‘n’ = 1

Hence the equivalent mass of $AgNO_3$ = 170 1 = 170.

FOR COMPOUNDS WHERE IODINE IS LIBERATED :

Let us consider the reaction of Copper sulphate with Potassium iodide in presence of Acetic acid as shown below.

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO4 + I_2$$

From the reaction it is clear that

2CuSO4 → 2I (atomic equivalent of Iodine liberated)

There fore the value of ‘n’ = 1

Hence the equivalent mass of $CuSO_4.5H_2O$ = 248 1 = 248.

FOR OXIDISING AND REDUCING AGENTS :

In oxidation reaction one or more electrons are removed and in reduction reactions one more electrons are added to the reacting species. There fore in this type reactions the value of ‘n’ is equal to the number of electrons gained or lost.

$$\text{Equivalent mass} = = \frac{\text{Molecular mass}}{\text{number of electrons lost or gained}}$$

In an oxidising reaction the oxidising agent $KmnO_4$ gets reduced to itself as shown below.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

In the above reaction the Manganese ion in +7 state is reduce to +2 state by absorbing 5 electrons .

Therefore the value of ‘n’ in this reaction is = 5

$$\text{Hence the equivalent mass of KMnO} = \frac{158}{5} = 31.6$$

FOR A REDUCING AGENT :

The reaction of the reducing agent Oxalic acid can be explained which takes part as follows.

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

Here the reactant releases two electrons. So ‘n’ = 2.

Therefore equivalent mass $H^2C^2O_4.2H_2O$ = 126 2 = 63.

THEORY OF INDICATORS :

INTRODUCTION

Before entering in to the theory of indicators let us know some technical terms as follows.

EQUIVALENCE POINT :

This is the stage in a titration at which the amount of titrant is exactly and stoichiometrically equivalent to the amount of analyte in the given sample.

For example in the titration of NaCl with AgNO3 the equivalence point is reached when exactly one ,mole of Ag^+ ions are added to each mole of Cl^- ion present in the solution of analyte.

The equivalence point in a titration is a theoretical one and can’t be realised or visualised physically.

END POINT :

The end point in a titration represents the point of completion of reaction where there is a characteristic change of physical properties . The end point is at or close to the equivalence point.

Thus the end point can be physically observed. Normally the end point is attained by the addition of a drop or two of the titrant. For accurate results the additional volume should be less as possible.

INDICATOR :

An indicator is a chemical substances that is added to the solution of an analyte to produce an observable physical change, mainly the change of colour at or close to the equivalence point.

Usually the indicator used are in solution form. The end point and the equivalence point need not be the same.

THEORIES OF ACID - BASE INDICATORS :

In neutralisation reaction the end point detection is based on the abrupt change in p^H value that occurs near the equivalence point. Such a change in p^H is dependent on the nature and concentration of analyte and the titrant. An indicator selection for this type titration can be done only with proper knowledge of the p^H changes that occur in the titration.

Ostwald’s theory gives an explanation to the colour change of indicator with the change in p^H.

According to this theory a hydrogen ion indicator is either a weak organic acid or a base. The undissociated molecule has one colour and its dissociated ion has another colour.

Let us explain this ionisation by taking HIn as the example as follows.

$$\underset{\text{colour - A}}{HIn} \rightleftharpoons \underset{\text{colour - B}}{H^+ + In^-}$$

That is the undissociated indicator HIn has colour A and the dissociated ion has the colour B.

The equilibrium constant of this dissociation is given by,

$$K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

where K_{In} is the indicator constant.

Since HIn and In^- has different colours the actual colour of the indicator will depend upon Hydrogen ion concentration.

There fore if concentration of H^+ is higher the concentration of HIn increases (since K_{In} is a constant). As a result the indicator shows predominantly colour A the acidic colour. On the other hand if OH^- concentration is high then the dissociation will be higher to give more of In^- . So now the indicator will predominantly have the colour of In^- that is the colour B the basic colour.

This is the mechanism of change of colour of the indicator in acid and basic media .

e.g.

The above phenomenon can be best explained by taking phenolphthalein.

Phenolphthalein being a weak organic acid under goes the following dissociation.

$$HPh \rightleftharpoons H^+ + Ph^-$$

colourless pink colour

In acid medium the H^+ ion concentration suppresses the forward reaction thus favoring the backward reaction. As a result phenolphthalein exists in predominant concentration and the solution is colourless.

On the other hand in presence of OH^- the concentration of H^+ decreases by favouring the forward reactions. As a result more and more of In- is formed and the indicator will be pink in colour.

e.g. 2.

Methyl orange is an organic base which dissociates as follows.

MeOH Me^+ + OH-

Yellow red

In basic medium the reverse reaction is favoured and hence the indicator will be yellow in colour.

On the other hand in acid medium the forward reaction is favoured giving a red colour to the indicator.

SELECTION OF INDICATORS :

It is important to choose the appropriate indicator for a particular titration .

For a strong acid and a strong base.

In this type of titrations the equivalence point appears at a p^H of 7 to 9. There fore any indicator like Methyl orange, Methyl red, Phenolphthalein etc. can be used which are efficient for p^H values of 4 --10.

For strong acid and a weak base

In these titrations the equivalence point is best attained at p^H value ranging from 6 to 4.

There fore Methyl orange and Methyl red which are effective at p^H values 3--4 and 4--6 respectively can be safely used.

But phenolphthalein whose range is 8---9 can't be used.

For weak acid and a strong base

In these titrations the equivalence point is more pronounced at p^H value of 8---10. There fore phenolphthalein which is effective in the range of 8--10 can best be used.

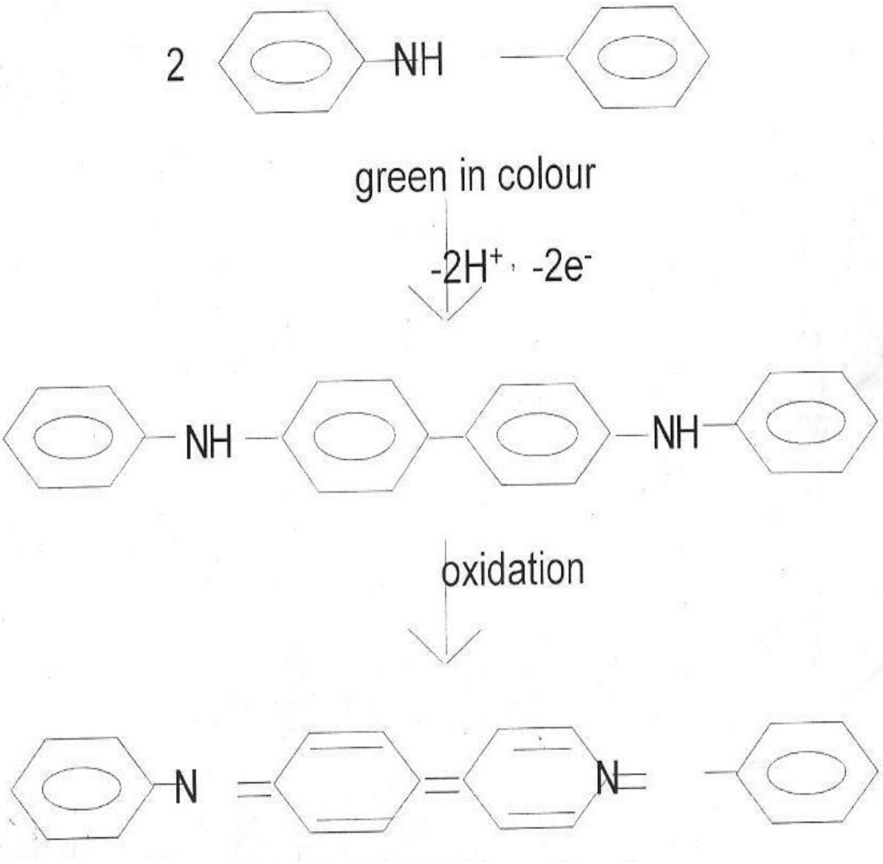
THEORY OF REDOX INDICATOR :

The theory behind redox indicators is the indicator has one colour in the ordinary or reduced state and another colour in the ixidised state.

For example let us consider the redox titration of Potassium dichromate with Ferrous sulphate or Ferrous ammonium sulphate.

In this titration diphenylamine is used as an internal indicator. The indicator is light green in colour in the ordinary condition. But it is violet in colour when in the oxidised state.

As long as Ferrous ions in the analyte react to give Ferric ion on the addition of $KMnO_4$, the indicator is not at all affected. But as soon as all the ferrous ions are changed to ferric ions, the addition of a single drop of dichromate oxidises diphenylamine indicator in to Biphenyl benzidine which is violet in colour, as shown below.



THEORY OF ADSORPTION - FLUORESCEIN INDICATOR :

This theory can be explained by taking the titration of Sodium chloride against Silver nitrate.

In this titration an adsorption indicator namely fluorescein is used. Up to the equilibrium point, the precipitate of AgCl absorbs Cl- ions present in excess of the solution. Now the fluoresceinate ion being -ve is repelled by -vely charged AgCl precipitate surface. At this stage the solution is yellowish green in colour due to fluorescein.

At equilibrium point all the Cl- is absorbed by Ag^+ and further addition of Ag^+ is absorbed by the AgCl precipitate surface which becomes +ve. Now the fluoresceinate ion is absorbed by the precipitate surface and Silver fluoresceinate is deep red in colour which shows the end point of the titration.

EXERCISES :

1. How would you prepare ,

   a). 2 liters of 0.5 molar hypo solution (molar mass of hypo = 278).

   b). 100 ml of 0.1M solution of Mohr's salt (molar mass of Mohr's salt = 392).

2. Calculate the molality of a solution containing 4.6 gm of ethanol in 100 gm of water.
3. Calculate the amount of Oxalic acid to be taken for preparing 250 ml of 0.25 N solution. (equivalent mass of Oxalic acid = 63)
4. Calculate the equilibrium mass of $K_2Cr_2O_7$ which gives the following reaction.
5. $Cr_2O_7 + 14 H^+ + 6e^- \longrightarrow 2Cr_2^{3+} + 7H_2O$
6. What will be equivalent mass of Sodium thiosulphate using a iodometric titration reaction.
7. Using the principle of volumetric analysis calculate the normality of 20.7 ml of HCl which react completely with 22.1 ml of normality 0.0987 N, NaOH.

EXPECTED QUESTIONS :

1. How filtration is done in semi micro method?
2. What are the advantages of semi micro analysis?
3. Why ammonium radical is placed in a separate group?
4. Give the principle behind the Sodium carbonate extract.
5. How does macro analysis differ from semi micro method?
6. Which concentration term is used in volumetric analysis?
7. Define equivalent mass.
8. What are indicators?
9. Write a note on adsorption fluorescein indicator.
10. Give the principle of volumetric analysis.

NOTES

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

UNIT -- III

INTRODUCTION :

Unit - III deals with mainly Organic chemistry. To start with electron displacement effects are discussed .

Then inter molecular forces and its effect on physical properties like melting point boiling point etc. are given importance.

Then active reaction intermediates like carbene carbo cation and their uses in chemical reactions are dealt with.

Then comes Cyclo alkanes its preparation and their stability based on Bayer's strain theory is discussed.

Then importance is given for reaction mechanism and its studies.

Finally we will discuss the addition reactions of alkenes and different rules that govern addition reactions are discussed.

ELECTRON DISPLACEMENT EFFECTS :

ELECTRON DISPLACEMENT :

Let us take the covalent molecules namely H_2, Cl_2 and HCl which have the following structures.

H H Cl Cl H Cl

In H_2 and Cl_2 the covalent bonds are shared by similar atoms namely Hydrogen and Chlorine respectively. So the atoms carrying the bonds having the same electronegative values attract the bonded electrons with equal effort. As a result the electron density will not move toward any of the atom and hence the electron density will be at the centre of the molecule.

Due to this, both the atoms are neutral and such a bond is called pure covalent bond and such molecules are called homo diatomic molecules.

But in the case of HCl the covalent bond is shared by two dissimilar atoms namely Hydrogen and Chlorine. The electro negativity of these two atoms are different. Since Chlorine has more electronegativity it attracts the bonded electrons more towards itself and as a result of this, Chlorine atom attains a partial +ve charge and the Hydrogen atom attain a partial -ve charge. This effect can be shown as follows.

H Cl

This type covalent bonds are called the polar covalent bonds and this type molecules are called the hetero diatomic molecules.

This permanent electron displacement in compounds which produce remarkable changes in its physical and chemical properties is called the electron displacement effects.

Electron displacements can be classified as follows. They are

1. Inductive effect,
2. Inductomeric effect,
3. Steric effect,
4. Mesomeric effect,
5. Resonance,
6. Hyper conjugation and

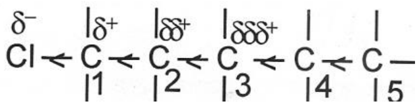
The permanent displacement effects like inductive and mesomeric effects are called also polarisation effects.

INDUCTIVE EFFECT :

The permanent polarity induced on the carbon skeleton and the substituent attached to it, due to minor displacement of bonding electron pair, caused by electronegativity difference of atom or group, which affects the physical and chemical properties of that compound is called the Inductive effect.

Illustration:

Let us consider the following carbon skeleton to which a chlorine atom is attached at the one end.



Since Chlorine is more electronegative than Carbon it attracts the bonded electrons toward it self as shown in the diagram, indicated by the arrow marks. As a result of this displacement of electrons the more electro negative Chlorine atom attains a partial negative charge and the C1 atom attains a partial positive charge. Now due to the partial +ve charge gained by the C1 atom it becomes more electro negative than the C2 atom though both of them are the same. As a result the C1 C2 bonded electrons move toward the C1 making C2 partially +ve but the charge is less than that of C1. In a similar way C3, C4 and so on atoms also get +ve charges.

This effect which produce a remarkable change in properties of the compound is called the *inductive effect* .

The inductive effect is denoted by I. There are two types of inductive effects namely +I and -I effects.

The inductive effect where the electron density is supplied to the carbon skeleton is called the +I effect.

The +I groups with their decreasing order or strength can be represented as given below.

$O\text{-}>COO\text{-}>R_3C\text{-}>R_2CH>RCH_2>CH_3>H$

The inductive effect where the electron density is pulled away from the carbon skeleton is called the -I effect and the -I groups with their decreasing strength can be shown as follows.

$-NR_3^+>SR_2^+>NH_3^+>NO_2>F>Cl>Br>I>OCH3>C_6H_5>H$

***CHARACTERISTICS OF INDUCTIVE EFFECT* :**

1. It is permanent effect.
2. Acts on the □□bond only and it is a weak one.
3. The charge displacement in only partial and not fully.
4. The strength of this effect goes on decreasing with the increase in the length of carbon and it can be presumed to be nil after the second carbon atoms.
5. The direction of electron displacement is indicated by the arrow marks as shown in the example.
6. Though the electrons are displaced permanently , the electron pair remains in the same valence shell.

APPLICATIONS :

PHYSICAL PROPERTIES

Bond length.

The presence of inductive effects in certain compounds makes change in their bond lengths.

For example in Methyl halides the bond lengths are lower than that of expected one on the basis of atomic radius. More over the bond lengths go on decreasing as the strength of the inductive effect goes on increasing. The bond lengths and the corresponding compounds can be represented as follows.

Compound :	CH_3 I	CH_3 Cl	CH_3 Br	CH_3 F
Bond length :	$2.1A^o$	$1.94A^o$	$1.78A^o$	$1.38\ A^o$

We know the inductive effect of halogens goes on increasing as we pass from fluorine. As a result the ionic character of the bonds also increases which shortens the bond length. Hence the decrease in bond length as shown above.

Dipole moment.

The dipole moment of Methyl halides can be represented as follows.

Compounds	$CH_3 \to I$	$CH_3 \to Br$	$CH_3 \to Cl$
Dipole moment :	1.6D	1.79D	1.83D

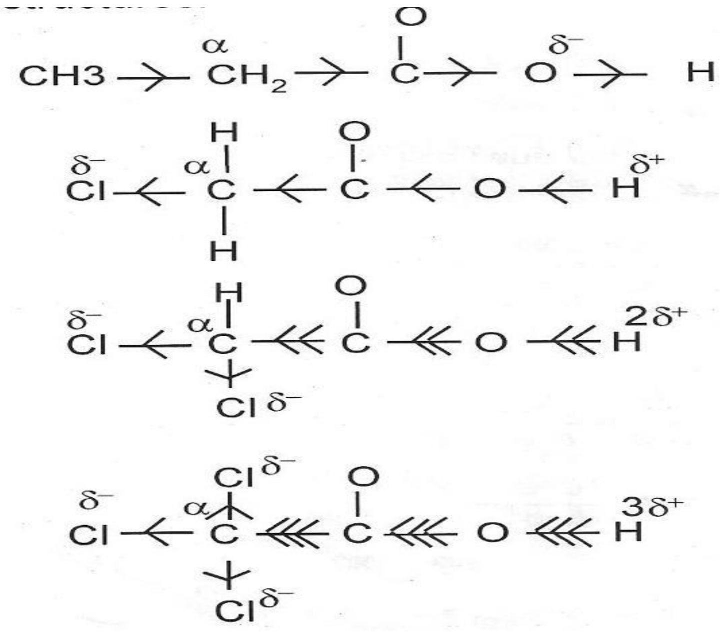
We know that the dipole moment of the compounds depends on the density of charge separation and the distance between the two poles. In the above examples it is clear that the intensity of charge separation goes on increasing due to the increase in the inductive effects of the halogen atom.

As a result the dipole moment values goes on increasing as we pass from the left to the right.

CHEMICAL PROPERTIES :

Acidity of acids.

Let us consider the acidities of Acetic acid, Chloro acetic acid, di chloro acetic acid and tri cholro acetic acids which has the following structures.



In Methyl acetic acid the methyl group attached to the carbon atom of the -COOH group having +I effect, increases the electron density at the Hydrogen atom and as a result it acquires a partial negative charge. Hence it looses its electro positivity which is essential for acidic character. Thus the Methyl group which has +I effect attached to the carbon of -COOH decreases the acidic character.

On the other hand in mono chloro acetic acid the chlorine atom attached to the carbon atom having a -I effect pulls the electron density from the carbon skeleton and as a result the H - atom of the - COOH group gets a partial positive charge. This property increases the acidity of mono chloro acetic acid.

In di chloro acetic acid, there are two chlorine atoms at the

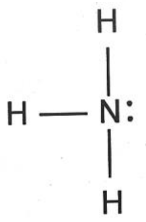
carbon atoms with - I effect which makes the H - atom more +ve making the di chloro acetic acid more acidic than methyl acetic acid and mono chloro acetic acids.

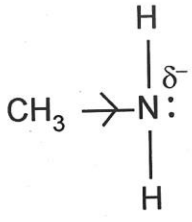
In a similar way the acidity of the tri chloro acetic acid also increases and it is the most acidic of all the above four acids.

Thus it is clear that a + I group attached to a - COOH group decreases its acidity and - I group increases its acidity.

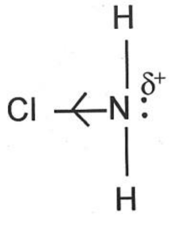
Basic strength of Amines.

Let us compare the basic strengths of the following amines namely Ammonia for reference, Methyl amine, chloro amine and Fluoramine which have the following structures.

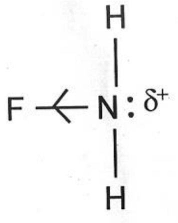

(1)



(2)



(3)



(4)

The Nitrogen atom in all the compounds are having a lone pair of electrons which is responsible for their basic nature.

In compound - (1) all the atoms surrounding nitrogen are Hydrogen which has no + I or - I effect. That is they can’t attract or supply electrons. As a result the electron density on Nitrogen atom is not changed.

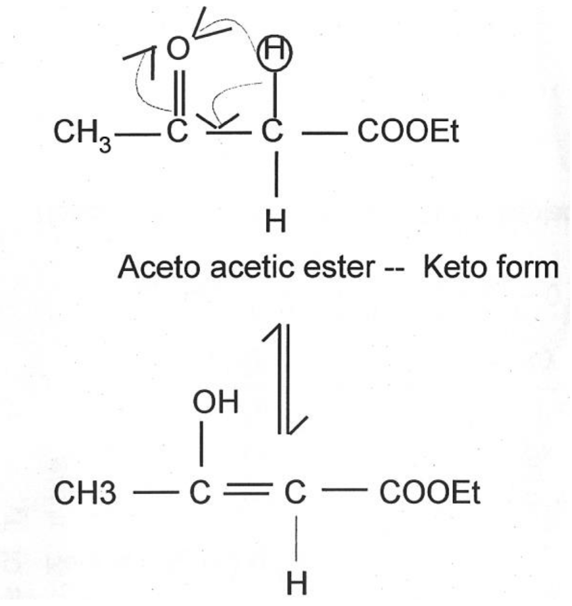
But in Methyl amine -(2) the methyl group attached to the Nitrogen atom due to its +I effect increases the electron density at the Nitrogen atom and as a result the Nitrogen atom acquires a partial negative charge is indicated. This phenomenon increases the basic strength of Methyl amine.

On the other hand in (3) and (4) the chlorine and Fluorine attached to the Nitrogen atom have -I effect which reduces the electron density thus making N - partially +ve. As a result the basic strength of these two compounds is lower than that of Methyl amine and Ammonia.

Among Chloramine and fluoramine, Fluoramine is less basic than Chloramine since florin is more electro negative than chlorine which makes the Nitrogen in Fluoramine more positive.

Enolisation.

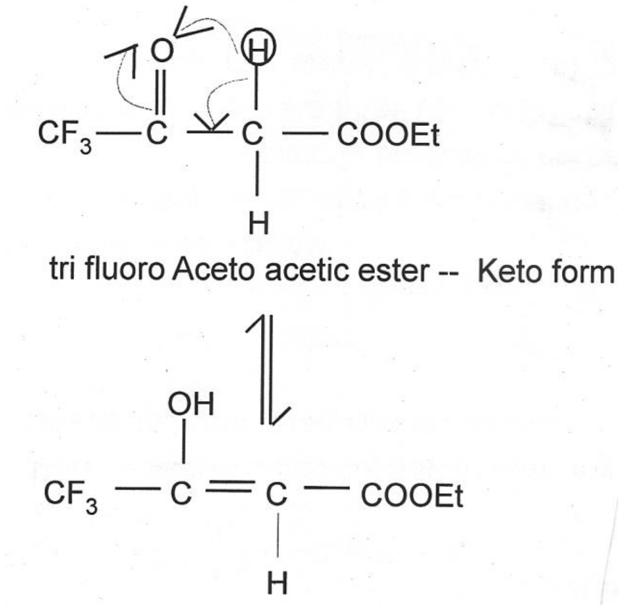
Let us consider the enolisation reactions of Aceto acetic ester and tri fluoro Aceto acetic ester as shown below.



Aceto acetic ester -- Enol form (7.5 % at room temperature)

On the other hand in tri fluoro Aceto acetic ester the Fluorine atom being more electro negative and hence having a high -I effect it attracts the bonded electrons towards It. As a result the methylene Hydrogen atom becomes more active and labile in nature so that the enolisation takes place very easily and to a larger extent.

The - I effect created by the Fluorine atom and the electro displacement can be schematically represented as shown below.



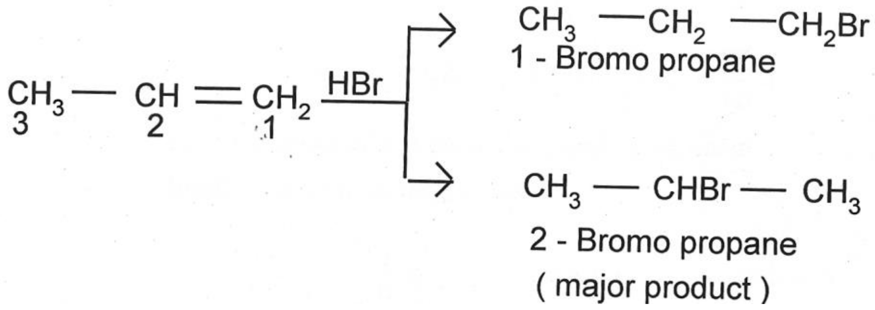
Tri fluoro aceto acetic ester-Enol form (89.0 % at room temperature)

Tri fluoro aceto acetic ester exists in 89 % enolic form at room temperature where as Aceto acetic ester exists in enolic form to as extent of 7.5 % only at room temperature.

In addition reactions.

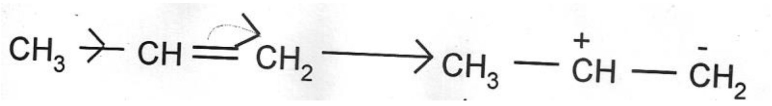
Let us explain this effect of inductive effect in addition reactions by taking the addition of HBr to 2 - Propylene.

Since this is an electrophilic reaction the H^+ of HBr can add to the C_2 or C_1 atom as shown below.



But the methyl group attached to the C_2 - atom, due to its +I effect, pushes the □ - electron towards C_1 - atom, making it negatively charged as depicted below.

+ -

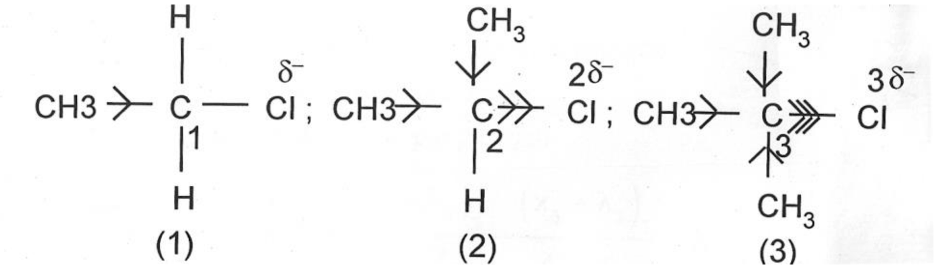


1 2 3

As a result of this the electrophile Br^+ adds to C_3 - atom giving 2 - bromo propene only as the main Product.

In substitution reaction.

Consider the compounds namely Ethyl chloride, iso - propyl chloride and tertiary butyl chloride which has the following structures.



In compound (1) there is only one methyl group attached to the C_1- atom which by its +I effect makes the chlorine atom partially negatively charged to some extent.

In compound (2) there are two methyl groups attached to the C1 - atom which by their inductive effect makes the chlorine atom little bit more negative than in (1).

On the other hand in compound (3) there are three methyl groups which by their +I effects make the chlorine atom the most negative.

As a result when we pass from left to right the ease of removal of chlorine goes on increasing and hence the rate of substitution reaction also goes on increasing.

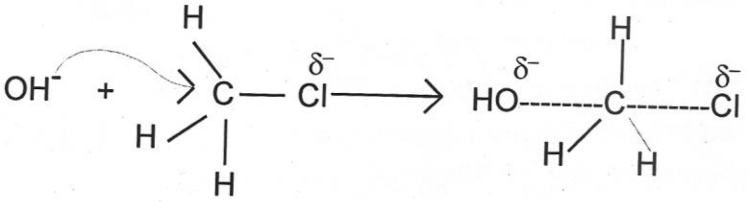
More over Ethyl chloride follows SN_2 mechanism, Iso propyl chloride follows both SN_1 and SN_2 whereas tertiary butyl chloride follows SN_1 mechanism.

INDUCTOMERIC EFFECT:

The enhancement of the inductive effect due to the presence of an attacking agent in a reaction is called the inductomeric effect.

e.g.

For example let us consider the reaction in which OH- ion attacks Methyl chloride as shown below.



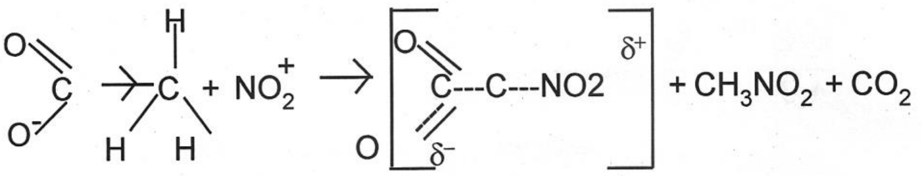
In Methyl chloride, chlorine atom with -I effect attracts the C - Cl bonded electrons towards itself. That is Cl atom is polarising the said bonded electrons.

But the attack by the OH- supplies the electron to the central carbon atom and there by to the C - Cl bond. As a result it becomes easier for Chlorine to pull the bonded electrons towards it. In other wards the OH- ion increases the polarisability of the bonded electrons .

This type of electron displacement effect which increases the polarisability of the bond is called the Inductomeric effect and also called the Inductometric effect. As it is a temporary or dynamic effect it is represented as I_D.

Since electron is supplied to the molecule it is called the $+I_D$ effect.

Another example where the electrons are pulled away from the molecule can be cited as follows.



This type of inductomeric effect where the electron density is pulled away from the molecule is called the $-I_D$.

CHARACTERISTICS :

1. Since the inductomeric effect operates only at the time of an attacking agent, this effect only enhances the reaction and never inhibits a reaction.
2. It is a dynamic or a temporary effect.

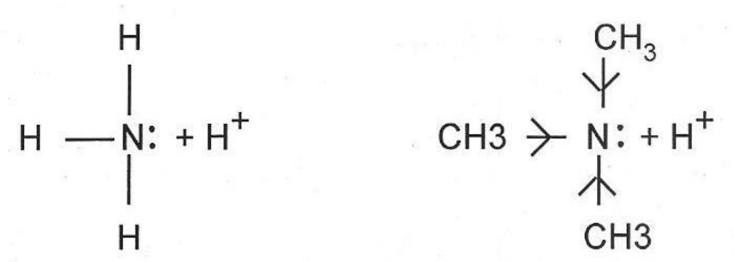
3. Since it aids the inductive effect, it has no separate applications.

STERIC EFFECT :

Bulky groups like $-CH_3$, $-COOH$, $-SO_3H$, -I and $-NO_2$ which occupy large area in space when present in a molecule, makes remarkable change in the properties of the molecule. This effect is called the steric effect.

e.g.

For example take the protonations of Methyl amine and tri methyl amine as shown below.



Though there are three methyl groups with +I effects in tri methyl amine it is less basic than Ammonia. It is because the tree bulky groups in tri methyl amine due to their steric effect hinders protonation.

Applications.

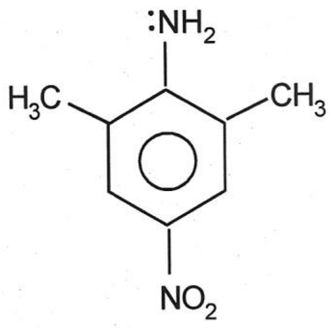
Basicity of aliphatic amines.

When we compare the basic strengths of ammonia, and tri methyl amine having structures as shown above ammonia is easily protonated in reaction with acids.

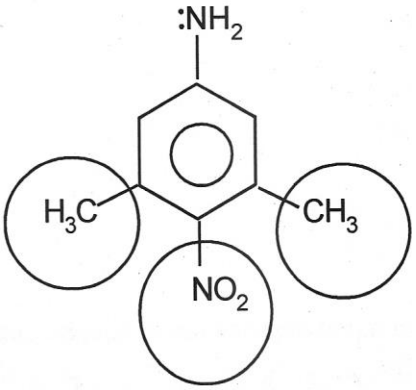
But in tri methyl amine the nitrogen atom which is responsible for basic nature is crowded by three bulky groups namely the methyl groups. As result the proton finds it very difficult to approach the nitrogen atom. Hence it is a weak base as compared to ammonia.

Basic nature of aromatic amines.

Let us consider for example 2,6 - dimethyl - 4 nitro aniline and 3,5 - dimethyl - 4 - nitro aniline having structures as follows.



(1)



(2)

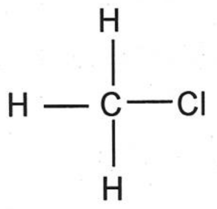
Both the compounds are basic in nature due to the presence of a loan pair of electrons in the -NH$_2$ group. But in compound (1) is less basic than (2), due to the following reason.

In (1) the nitro group present in pare position to the amino group under goes effective mesomeric effect so that it pulls the lone pair of electrons on nitrogen atom. As result the electron density available for protonation is decreased and hence its basic strength decreases.

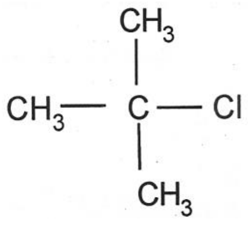
But in (2) the two methyl groups at the meta positions due to their larger size pushes the nitro group out of plane of the benzene ring and as a result the resonance here is highly inhibited which is called steric inhibition of resonance. Thus since the nitro group is not able to participate mesomerism with the benzene ring the electron density on the nitrogen atom is not at all affected. There fore compound (2) is more basic than that of (1).

In substitution reactions.

Consider the compounds methyl chloride and tertiary butyl chloride as shown below.



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}Cl}$$



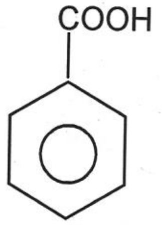
$$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}Cl}$$

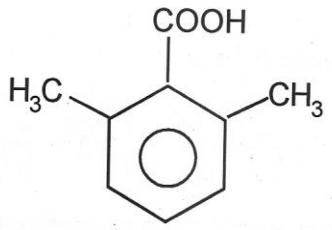
In methyl chloride the central atom which is free from steric strain has reasonable stability. But in tertiary butyl chloride the central atom is surrounded by three bulky methyl groups and due to this crowding the compound becomes less stable.

There fore in substitution and elimination reactions tertiary butyl chloride reacts very faster, in order over come the instability.

Steric hindrance.

Consider the esterification reactions of benzoic acid and 2’6 - dimethyl benzoic acids having the following structures.





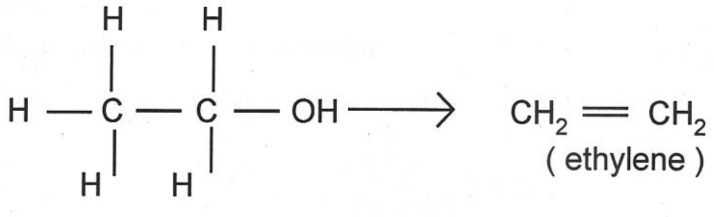
In benzoic acid the COOH group is free for attack by any group and hence the alcohol group can easily approach it and give an ester .

On the other hand in o, o - dimethyl benzoin acid the two bulky methyl groups at the ortho position hinders the approach of the alcoholic group thus preventing the esterification.

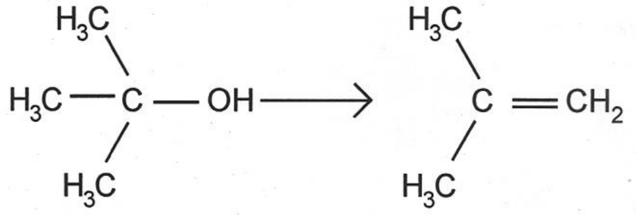
This effect is called the steric hinderance which prevents the normal chemical reactions of certain compounds.

Steric acceleration.

To explain this phenomenon let us take methyl ethyl alcohol and tertiary butyl alcohol undergoing elimination reactions as detailed below.



Ethyl alcohol



tertiary butyl alcohol iso butylene.

When ethyl alcohol is converted to ethylene there is no much difference in sterric strain between the reactant and the product and hence no much difference in stability of the two compounds.

On the other hand if we consider tertiary butyl alcohol, there is much difference in steric effect and hence in the stability of the reactant and the products.

There fore tertiary butyl alcohol undergoes elimination so many times faster than ethyl alcohol. This phenomenon is called the steric acceleration in chemical reactions also.

RESONANCE :

When no structural formula of a compound is able to explain satisfactorily all of its properties, then a combination of two or more structures was assigned, which can explain all the properties satisfactorily. This is called the mesomerism meaning between the parts or the intermediate structure (in Greek meso means between and mer means parts.)

In 1926 Heisenberg from quantum mechanics, supplied a theoretical back round for mesomerism and there after he called it resonance.

There fore the concept of hybridisation of two or more conventional valence bond structures to yield a new stable hybrid form with less energy which explains the properties satisfactorily is called resonance.

e.g.

Resonance came in to operation when Kekule's structure for benzene was found unsatisfactory in explaining its properties.

kekule assigned the following structures to Benzene.


(1)


(2)

Resonance in carbondioxide.

But later it was discovered that there are numerous compounds like benzene which can be assigned a hybrid structure.

e.g.

For example carbon di oxide has the following conventional structure.

O C O

Butt carbon dioxide was found to be more stable to an extent of 132. 2 kJ than that would be expected on theoretical basis. Similarly the actual bond length between carbon and oxygen was found to ne 1.15 A^{o} where as expected one is 1.2A^{o}.

There fore the following structures are assigned to carbon di oxide.

O C O   O C O   O C O

(1)   (2)   (3)

All these three structures are called the canonical structures and each structure contribute to some extent . There fore carbon dioxide has a hybrid structure of all the above three structures as represented below.

O C O

Another best example is that of benzene for which Kekule assigned the following two structures.

Resonance in Benzene.

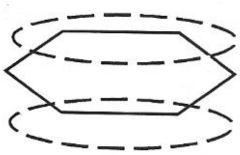
These structures imply that , in benzene there must be three C C double bonds and three C C single bonds. The calculated value of double bond length was found to be 1.33A^{o} and that of singly bond length was found to be 1.54A^{o} . But in benzene all the six bons were found to be equal to 1.39A^{o} which lies in between the single and double bond length.

Secondly, benzene was found to be more stable to an extent of 150.6 kJ than that of expected one on the basis of enthalpy calculations.

Thirdly, even though there are three double bonds in benzene it does not undergo any of addition reactions like alkenes. Benzene takes part only in substitution reaction reactions like the saturated compounds.

All these facts are not able to be explained by the old valence bond structures(1) or (2). Therefore benzene was assigned the following resonance structures.

That is all the unhybridized $2p_Z$ orbitals of the 6 carbon atoms in benzene overlap with each other to give a single molecular orbital as shown below.



Such a bonding orbital where the bonded electrons are not localised on any particular atom are called the de localised bonding orbitals.

Due to this delocalisation of orbitals the molecule attains unexpected stability. More over all the c- c bond lengths are equal.

Characteristics of resonance.

All the structures taking part in resonance are called the canonical forms or contributing structures or resonance structures.

All the resonating structures are related by double headed arrows as shown in the diagram.

Due to this resonance, energy is released and hence the molecule is stabilised to a large extent.

The energy released due to resonance is called the resonance energy.

As the number of canonical structures increases the stability of the molecule also increases.

Non polar forms are more stable than the polar forms.

It is a permanent effect and no assistance by any group is needed to initiate resonance.

Conditions for resonance.

All the atoms that take part in resonance must be coplanar. If the coplanarity is violated then the resonance will be less effective.

The energy of all the molecular orbitals taking part in resonance must be equal or more or less equal.

All the atoms or the molecule taking part in resonance must be present in identical places in all the forms.

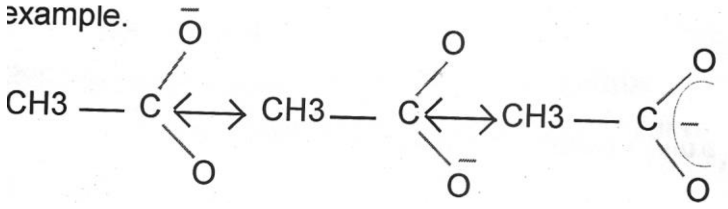
All the canonical forms must have equal or more or less equal energy.

The electron density in all the forms must be equal.

One form must be converted to the other by a single or more electron displacements.

The canonical forms must have the maximum number of bonds.

Other example.

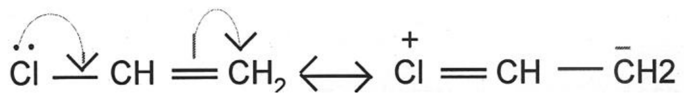


MESOMERIC EFFECT:

Though resonance and mesomerism look like the same, strictly speaking mesomerism is different from resonance.

The mesomeric effect may be defined as “ *the permanent polarisation or permanent displacement of electron pairs in a multiple bonded system* of the type Z C C .

e.g.

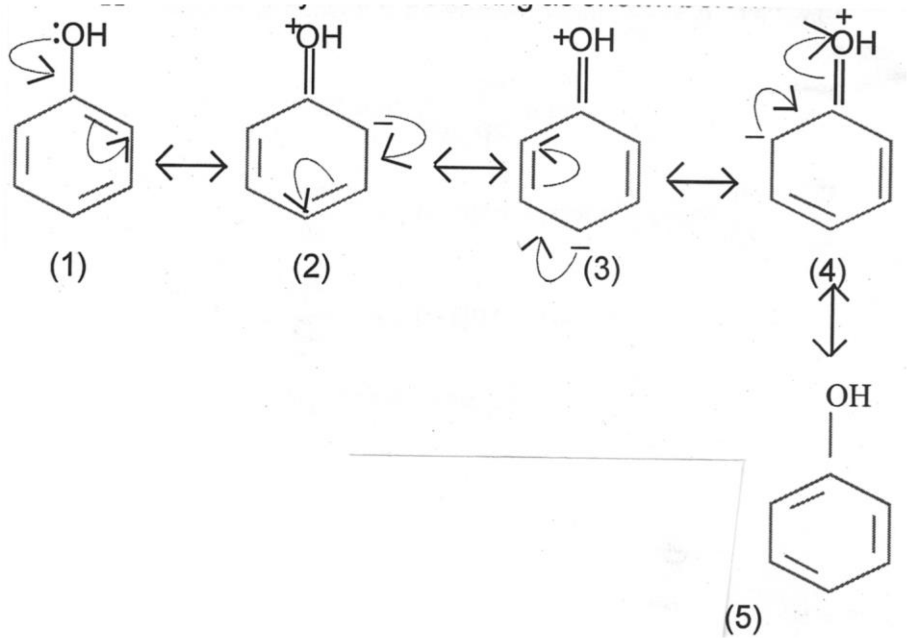


Thus in mesomeric effect the electron displacement is initiated by a loan pair of electrons and then relayed through electrons.

Mesomeric effect is represented by the symbol M and some times by R also. If the electron displacement is away from the group then it is called + M effect or +R effect and if the electron displacement is towards the group then it is called the -M or -R effect. These can be explained by the following examples.

Example for +M group.

In phenol the lone pair of electrons present on oxygen atom initiate the electron displacement, which is relayed through the conjugated electron density in benzene ring as shown below.



Structure (1) is the starting form of mesomerism and since electrons are displaced away from the oxygen atom it is called the +M effect.

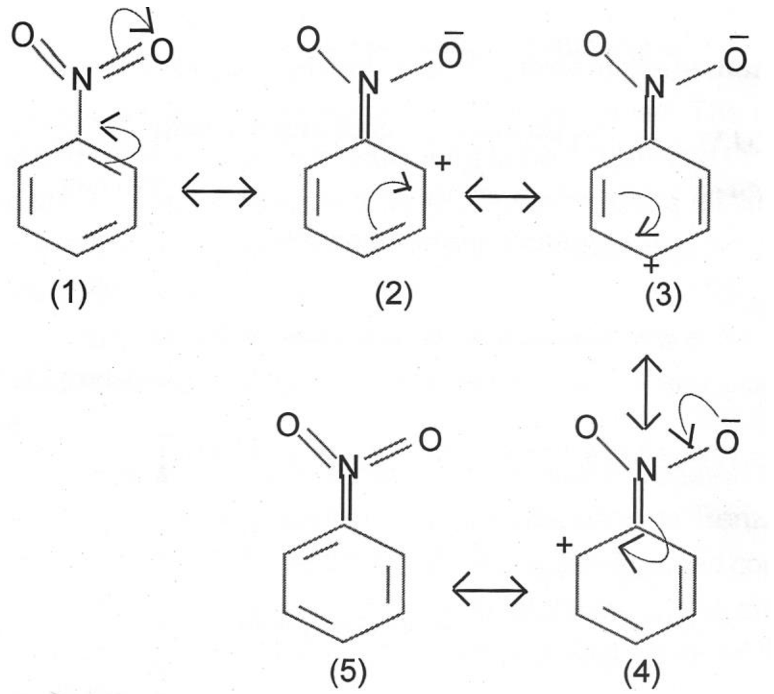
As a result of +M effect the electron displacement makes the two ortho positions and the para positions to carry a negative charge as can be seen from the structures (2), (4) and (3) respectively.

This makes the benzene ring of phenol to be more reactive towards the electrophiles than benzene itself. That is the benzene ring or phenol is activated because of +M effect.

More over the incoming electrophiles for example NO_2 preferably attacks the ortho or the para position of the benzene ring. That is +M groups orients the incoming electrophile to the ortho or the para position. Other +M groups are $-CH_3$, $-NH_2$, OMe, OEt etc.

Example for -M group.

Let us consider the mesomerism exhibited by nitro benzene as shown below.



The mesomeric effect is permanent effect and it extends to the full length of the carbon chain with full strength. That is the strength of the mesomeric effect is independent of length of carbon chain.

The nitrogen atom in the nitro group has spent all the five valence shell electrons for bond formation (but in the NH_2 group only three electrons are used for bond formation and two electrons are residing on nitrogen as the lone pair). Since there is no electron pair on the nitrogen atom, being more electronegative than the carbon atom it attracts the - electron away from the benzene ring towards it self. Therefore it is called the -M effect.

As a result of it, as seen from the structures (2), (4) and (3) a positive charge is developed on the two ortho and the para positions. On the other hand the electron density on the meta position is not affected. Therefore,

The benzene ring in nitro benzene is deactivated when compared to benzene itself. Hence nitro benzene undergoes electrophilic substitution at a lower speed as compared to benzene.

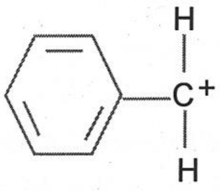
More over the incoming electrophile goes to the meta position only because this meta position is not at all affected.

Thus a - M group attached to the benzene ring deactivates the benzene ring and orients the incoming nucleophile to meta position only.

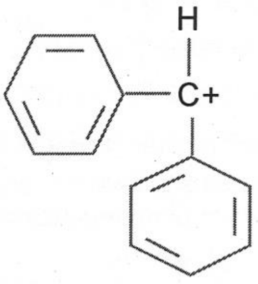
Application.

Stability of carbo cations.

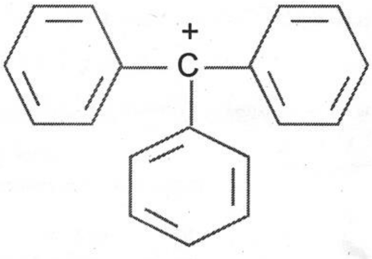
Let us consider the primary, secondary and a tertiary carbonium ions also called carbo cations which have the following structures.



1^{o} - carbonium ion

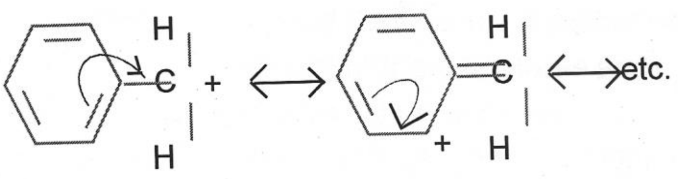


2^{o} - carbonium ion



3^{o} - carbonium ion

In the primary carbo cation there is only one phenyl ring attached to C+ ion. This phenyl ring under goes resonance or mesomerism as shown below.



phenyl methyl carbo cation

In a similar way there are five canonical forms possible in total.

For the above phenyl methyl carbo cation. We know that as the number of contributing structures increases the stability also increases. But for the secondary carbonium ion namely for bi phenyl methyl carbo cation there are ten canonical forms possible, five for each ring. There fore the secondary carbo cation is more stable than the primary one.

On the other hand in the case of triphenyl methyl carbo cation there fifteen structures are possible which makes it the most stable of these three .

Thus the stability of these three carbonium in the increasing order can be represented as follows.

1^{o}- carbonium ion < 2^{o} - carbonium ion < 3^{o} - carbonium ion.

In similar way the stability of 1o, 2^{o} and 3^{o} free radicals can also be established.

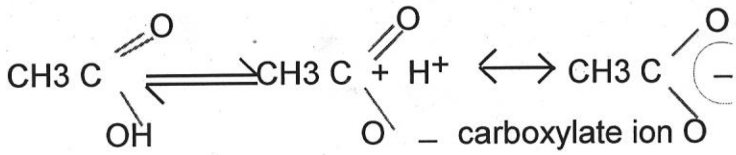
Acidity of carboxylic acids.

Though alcohol and the carboxylic acid groups posses -OH groups only the carboxylic acids behave as acids. This fact can be explained as follows.

Ethyl alcohol ionises as follows.

$$CH_3\,CH_2OH \rightleftharpoons CH_3\,CH_2\,O^- + H^+$$

The ionisation of carboxylic acid for example acetic acid, is as follows.



After the ionisation of the alcohol the ethoxide ion formed is not at all stbilised by any of the electron displacement effects. On the other hand the +I effect of the ethyl group destabilises the ethoxide ion. As a result of this the H+ ion ionised immediately reunites to the ethoxide ion to give alcohol again. There fore it can’t act as an acid.

But in the case of acetic acid the carboxylate ion formed after the ionisation gets stabilised by resonance. Thus the carboxylic acids act as acid because of the stabilisation of the carboxylate ion.

HYPER CONJUGATION : BAKER NATHAN EFFECT.

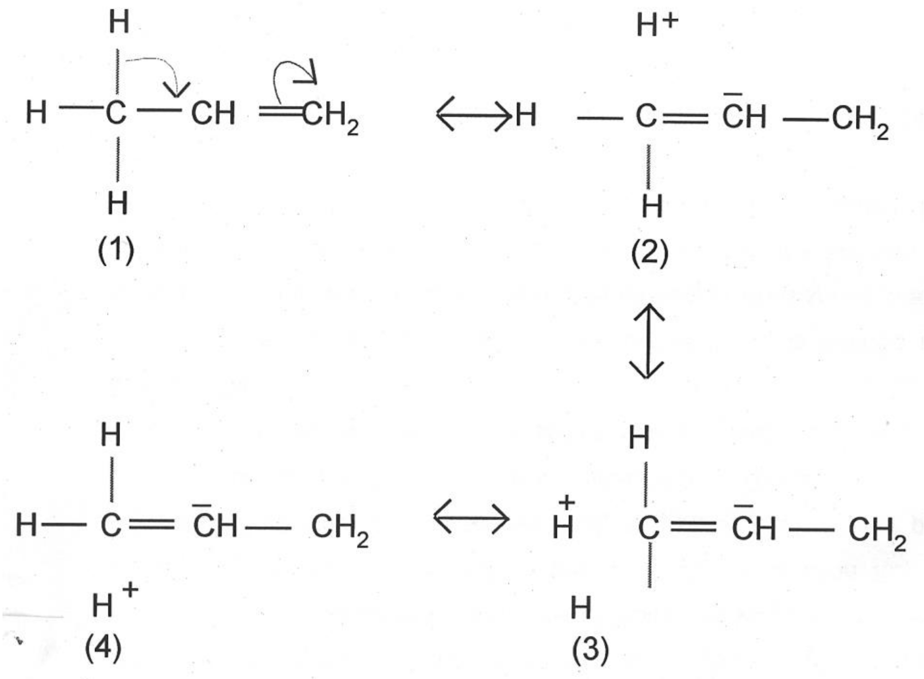
We know that the inductive effect of alkyl groups is in the following decreasing order.

That is tertiary butyl > iso propyl > methyl group.

But this order was reversed when these alkyl groups are attached to an unsaturated system of the type C C . To explain this behavior Baker and Nathan explained a new concept called hyper conjugation which states that,

“an electron displacement of C - H sigma bond electrons which are □□- to a double bond, towards the double bond.

The hyper conjugative effect can be explained as follows taking propylene as the example.



Baker and Nathan explained that this resonance happens due to the interaction between the - electrons of C - H bond of alkyl group and the pi - electrons of p - orbital .

Since there is no bond between the carbon and hydrogen of the alkyl group this resonance is also called the no bond resonance.

Characteristics of hyper conjugation.

Hyper conjugation takes place only when an alkyl group is attached to a multiple bonded carbon.

It is permanent effect.

It operates with full effect up to the last carbon present in a conjugated system.

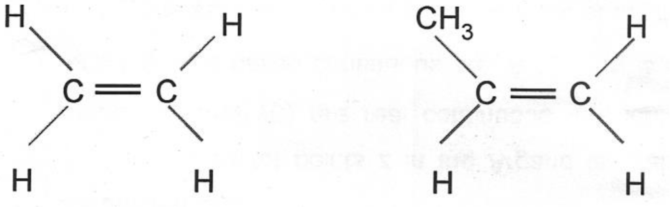
As the number of structures due to hyper conjugation increases the stability of the molecule also increases.

The energy released during hyper conjugation is called the hyper conjugation on no bond energy.

Applications of hyper conjugation.

Stability of alkenes.

We know that ethylene and propylene are having the same geometry as shown below.



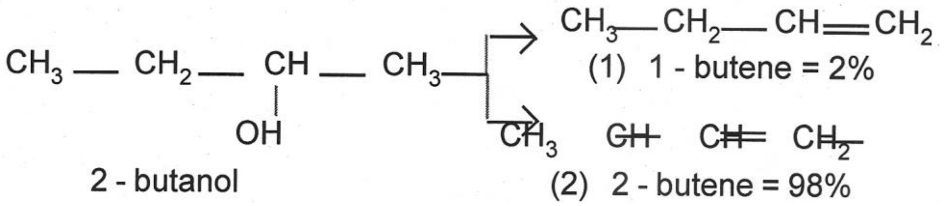
ethylene propylene

But from the heat of hydrogenation of ethylene is - 32.8 K cal where as that of propylene is - 30.1 k cal. This shows that propylene must be more stable than ethylene to an extent of 2.7 K cals.

This is because there is hyper conjugation in propylene which is not found in ethylene.

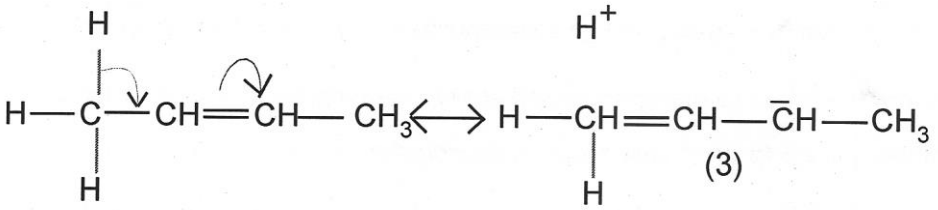
In elimination reactions.

Let us consider the elimination reaction of 2 - butanol in presence of concentrated sulphuric acid. It can yield 1 - butene or 2 - butene as shown below.



But in the above reaction actually 2 - butene was the major product obtained to an extent of 98 % where as 1 - butene was obtained only to an extent of 2 %.

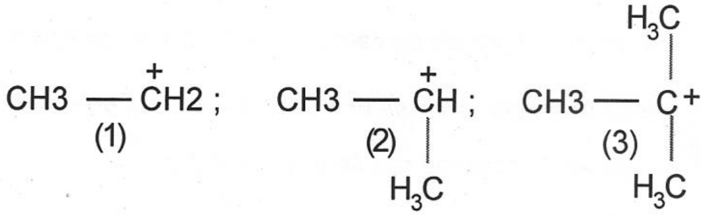
This is because in 2 - butene there are a total of six resonance structures as a result of hyper conjugation similar to that of the following one (3).



On the other than in 1 - butene there are three resonance structures are possible. But we know that more the number of resonance structures the more the stability of the compound.

Stability of carbo cations.

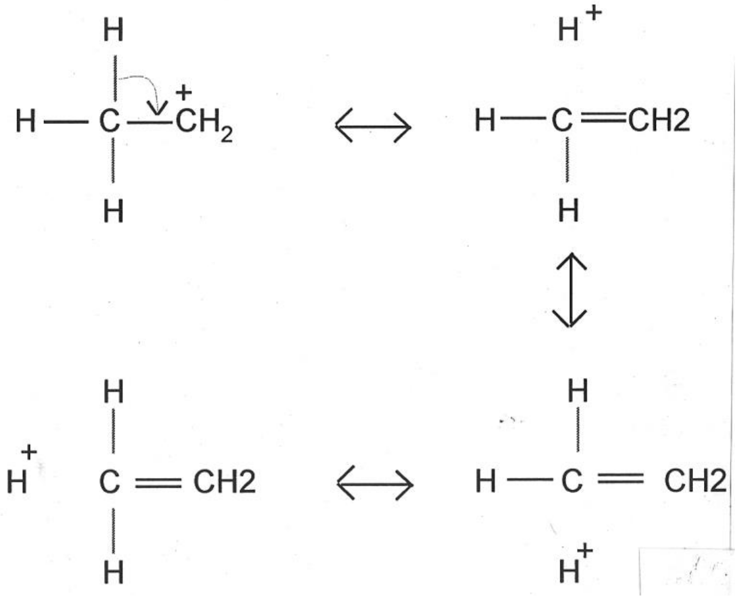
Let us consider the stabilties of ethyl, iso propyl and the tertiary butyl carbo cations which have the following structures.



$CH3 - \overset{+}{C}H2$; (1) $\quad CH3 - \overset{+}{C}H(H_3C)$; (2) $\quad CH3 - C^{+}(H_3C)(H_3C)$ (3)

The carbonium ions (1), (2) and (3) are primary , secondary and tertiary ones respectively.

In (1) there is only one methyl group, in (2) there are two methyl groups and in (3) there are three methyl groups in □□- to the carbon atom. In all the ions there is resonance because of hyper conjugation. For example we can draw the resonance forms for the carbonium ion (1) as shown below.



Thus we have a total of four canonical forms for (1). But for (2) we will have seven and for (3) ten resonance structures . We know that the stability increases with increase in the number of resonance forms. There fore the tertiary carbo cations is the most stable one. The increasing order of stabilities these carbonium ions can be represented as follows.

primary < secondary < tertiary carbonium ion.

Thus like resonance and mesomerism hyper conjugation also increases the stability of carbo cations.

Orientation effect in benzene.

A methyl group attached to benzene ring naturally under goes hyper conjugation which makes a +M effect. There fore hyper conjugation in benzene activates the ring and has ortho para direction nature like other +M groups.

(For resonance structures refer bond displacement of +M groups in benzene.)

LOCALISED AND DE LOCALISED CHEMICAL BONDS :

A covalent bond is formed between two atoms by the sharing electrons in pairs each atom contributing one.

The sharing takes place in order to full fill the octet configuration of electrons in both the atom so that they get stability. In this type of bond formation the shared pair of electrons are present at middle of the two atoms which make the co - valent bond as represented below in chlorine molecule.

$$Cl - Cl$$

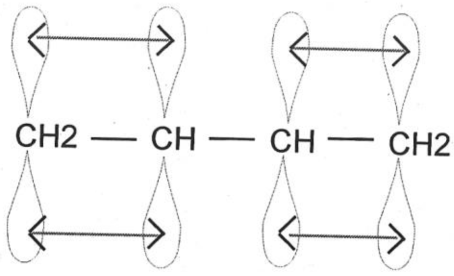
a localised bond

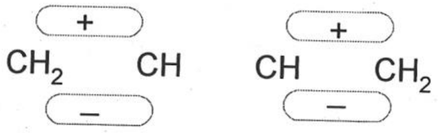
This type of bonds in which the bond pair of electrons are confined within the atoms forming the bond are called the localised bond. The bond pair of electrons are with opposite spin.

To explain delocalised bonds let us consider the bonding in 1,3 - buta diene which has the following structure.

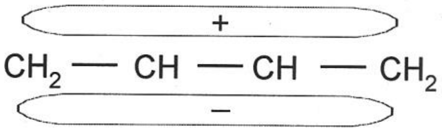
$$\underset{1}{CH_2} = \underset{2}{CH} - \underset{3}{CH} = \underset{4}{CH_2}$$

All the four carbon atoms in this compound are sp2 hybridised leaving the $2p_z$ orbitals free of hybridisation. The $2p_z$ orbital of C1 and C2 make an lateral overlap to give a pi - bond. Similarly C3 and C4 atoms too form another pi bond to form 1,3 - buta diene having the following pi - molecular orbitals.





But since all the $2p_Z$ orbitals carried by four carbon atoms have the same symmetry and same energy, there is a possibility of lateral overlaping among themselves. That is the $2p_Z$ orbitals of four carbon atoms overlap with one another to give a molecular orbital of the following type.



Here the four atomic orbitals give a single molecular orbital as shown in the above representation. Thus it is clear that the four electrons are not confined to any of the atom. That is they are not belonging any atom but common to all the atoms.

Such a type of bond in which the bond pair of electrons are not confined to any of the atom is called the delocalised bonds or a delocalised orbital.

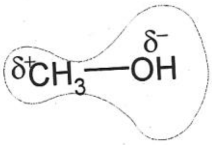
In a delocalised orbital or bond the electrons have freedom to move in large area. So the repulsive force between the electrons decreases and as result of it the stability of the molecule increases. This energy of stabilisation which is similar to the resonance energy is called the delocalisation energy. More over due to delocalisation the single bond length decreases and the double bond length increases.

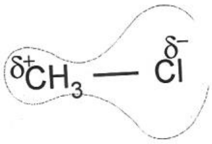
INTER MOLECULAR INTERACTIONS :

DIPOLE - DIPOLE INTERACTIONS :

In a non polar molecules like methane and ethane there will not be any charge separation on the atoms since both the atoms carrying the bond are similar. As a result there will be no dipole on the molecule.

But on the other hand in molecules like methanol and methyl chloride due to electronegativity differences among groups there is a charge separation and hence a dipole exists as shown below.





Thus in polar molecules there is an attraction between the positive end of one polar molecule and the negative end of another molecule and so on.

This type of interaction can be schematically represented as follows.

This type of interactive force in called the dipole - dipole interaction. As a result of this interaction polar molecules are more strongly held than the non polar molecules and makes a remarkable change in the physical properties of that compound. For example melting points, boiling points and solubility are affected which can be explained as follows.

Melting point.

In case of solids of high molecular weight fatty acids have high melting points than those of paraffins which have more or less equal molecular weights.

This is because in polar fatty acids the dipole - dipole interaction between the molecules holds the molecular units tightly and hence excess of energy is to be spent in order to break the molecular force of attraction.

Boiling points.

Similar to melting point, boiling points of polar compounds are also higher than that for non polar molecules(alcohol and alkanes). The reason is the same as that explained for melting point.

Solubility.

Solubility of polar molecules is high in a polar solvents and less in non polar solvents. This is because in polar solvents the presence of dipole is appreciated where as in a non polar solvent it is rejected. The attractive force between the molecule and the solvent increases thus decreasing the energy and increasing the stability.

It is also observed that the more the dipole - dipole interaction in the molecule the more its solubility in a polar solvent and less the solubility in a non polar solvent.

van der Waals forces.

In non polar compounds there will not be any dipole. But there is a weak inter molecular force due to the attraction between the nuclei of one molecule and the electrons of the other. There is also weak force of repulsion between the electrons and nuclei of one molecule with another. This type of forces are called the van der Waals forces or van der Walls London forces.

Characteristics of van der Waals forces.

The attractive and the repulsive forces are normally compensated with each other.

van der Waals forces are only short range forces and therefore significant only when the molecules are very closer to each other.

Therefore the larger the molecules, the greater the surface area, closer the molecule and stronger the van der Waals forces.

Applications

(Similar to that of dipole - dipole interaction)

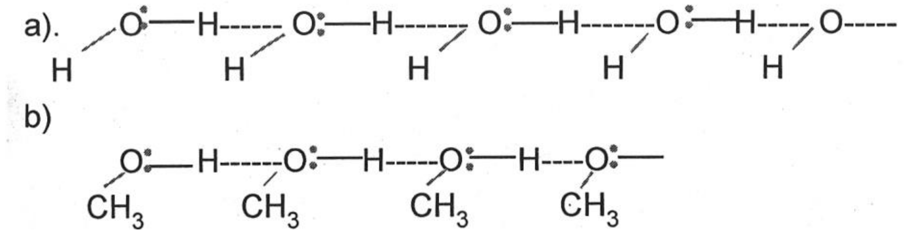
HYDROGEN BONDING :

Hydrogen atom linked to strongly electro negative atoms like N, O, F and Cl are called active hydrogen atom due to its more positive nature.

The partial dipole - dipole interaction between the active hydrogen and the strongly electro negative elements like N, O, F and Cl having at the least one loan pair of electron is called the hydrogen bond.

e.g.

The hydrogen bond in water molecule can be depicted as follows.



This hydrogen bonding is also called the hydrogen bridging or proton bonding.

Types of hydrogen bonding.

Hydrogen bonding can be classified in to two types namely ,

1. Inter molecular hydrogen bonding and

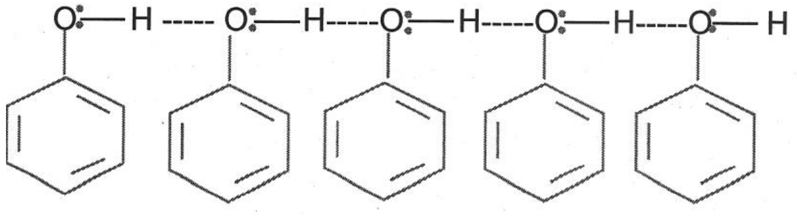
2. Intra molecular hydrogen bonding

which can be explained as follows.

Inter molecular hydrogen bonding.

The hydrogen bonding formed between two same or different molecule is called the inter molecular hydrogen bonding.

e.g.



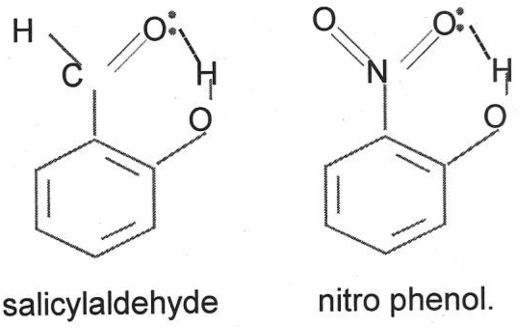
phenol.

Intra molecular hydrogen bonding.

Hydrogen bonding between the atoms within a molecule is called the intra molecular hydrogen bonding.

e.g.

For example the hydrogen bonding in salicylaldehyde can be cited as follows.



Characteristics of hydrogen bonding.

Here hydrogen acts as a bivalent atom and hence form a second co-valent bond.

The second co - valent bond is represented by dotted lines.

There fore bond length of hydrogen is greater than the normal bond length.

It is a weak bond with dipole - dipole interaction.

The hydrogen bond energy is around 8 to 42 kJs only.

Though it has low energy the hydrogen bonding has significant effect on certain physical properties like melting point, boiling point and solubility.

Other examples.

Water, alcohols, phenols, carboxylic acids, amines etc.

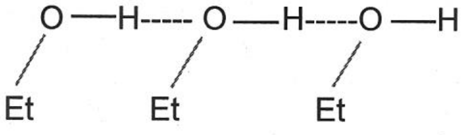
Applications.

Boiling point.

The smaller molecules which have more or less equal molecular weights must be having nearly same boiling points. It was found true in ordinary molecules. But the boiling points are unexpectedly high for molecules with hydrogen bonding as represented below.

Compound :	$CH_3 CH_2 CH_3$;	$CH_3 O CH_3$;	$CH_3 CH_2 OH$
Boiling point:	228 k	248 k	351 k

This is because in propane and ether there is no hydrogen bonding. But in ethyl alcohol hydrogen bonding as shown below.



This hydrogen bonding in ethanol gives extra stability to the molecule. More over before making it boil we have to supply extra heat energy to separate the molecules held by hydrogen bonding. These two factors are responsible for the higher boiling nature of alcohol.

Melting points.

Similar effect is also observed in melting points of solids with high molecular weights.

Solubility.

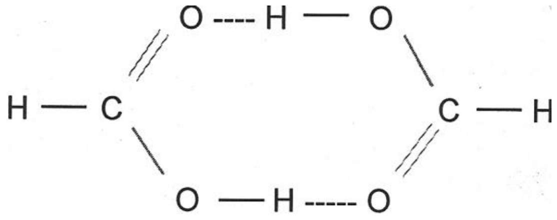
Lower alcohols dissolve in water because they form hydrogen bonding withe water. Similarly aliphatic aldehydes and aliphatic acids of lower molecular weight are freely soluble in water due to their nature on hydrogen bonding with water.

But molecules with higher molecular weights though they are capable of producing hydrogen bonds with water they are insoluble or sparingly soluble in water. It is because as the molecular weight increases the steric effect also increases which hinders hydrogen bonding. As a result their solubility decreases as the molecular weight increases.

Association of molecules.

The molecular weight determination of carboxylic acids by cryoscopic and vapour density methods gave twice the theoretical value.

For example the molecular weight of formic acid is only 46. But the value experimentally determined was found to be 92. This anomaly was attributed to the dimerisation of formic acid in the liquid state as shown below.



REACTIVE INTERMEDIATES :

Intermediates.

Intermediates are the chemical species which are used in chemical reactions. There are two types of intermediates which can be explained as follows.

Synthetic intermediates.

Synthetic intermediates are the stable compounds which can be prepared, isolated, purified, stored and used as and when they are needed.

For example in the synthesis of nitro benzene from acetylene, first of all acetylene must be passed through a red hot tube to get benzene and then benzene must be nitrated to nitro benzene.

In this reaction sequence benzene is the synthetic intermediate, which can be prepared and stored and consequently used.

Reactive intermediates.

Reactive intermediates are the highly reactive and short lived species which are formed in the course of chemical reactions.

They can’t be isolated hut can be trapped. Their knowledge is essential to assigning a mechanism to a chemical reaction.

Classification.

The reactive intermediates can classified as detailed below.

1. Carbo cations (carbonium ions)

2. Carbanions

3. Free radicals

4. Carbenes

5. Arenes

6. Benzynes and

7. Nitrenes.

Out of these reactive intermediates the first four are going to be discussed here.

Carbo cations.

In olden days these are called the carbonium ions. But normally the suffix ‘onium’ is assigned to cations in which the central atom have one valence more than its normal valency. For example the valency of nitrogen atom in NH_4+ ion is 4 and so it is called ammonium ion.

But in CH_3+ the valency of the central carbon atom is one unit less than its normal valency. There fore it is wrong to call it carbonium ion and hence now a days they are called the ‘carbo cation’.

An organic species which carries a +ve central carbon atom with sextet of electrons in its valence shell is called a carbo cation.

Carbo cations act as strong electro philic reagents. They are classified in to three types namely,

1. Primary carbo cation,

2. Secondary carbo cation and

3. Tertiary carbo cation as explained below.

If the carbon atom carrying the +ve charge is linked to only one carbon atom directly, then it is called the primary carbo cation.

e.g.

CH_3+ ; CH_3CH_2C+

If the carbon atom carrying the +ve charge is linked to other carbon atoms directly then it is called the secondary carbo cation.

e.g. $(CH_3)2CH+$

If the carbon atom carrying the +ve charge is linked to three other carbon atoms directly, then it is called the tertiary carbo cation.

e.g.

$(CH_3)3C+$; Ph_3C+

Generation of carbo cations.

Though it is difficult to isolate the carbo cations in most of the reactions, they are isolated freely or as ion pairs in certain cases. Carbo cations can be prepared by the following methods.

1. By direct ionisation.

In presence of highly polar solvents like SO2, most of the organic compounds under go self ionisation to give carbo cations as shown below.

$$(CH_3)_3Cl \xrightarrow[SO_2]{liquid} (CH_3)_3C^+ + Cl^-$$

Similarly in sulphur dioxide solvent ,alkyl fluorides react with the Lewis's acid namely antimony fluoride to yield carbo cations as shown below.

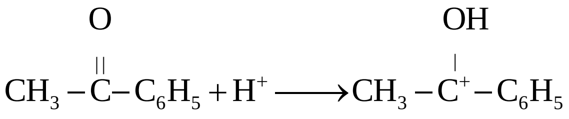
$$CH_3CH_2F + SbF_5 \xrightarrow[SO_2]{liquid} CH_3CH_2 + SbF_6^-$$

By this method secondary and tertiary carbo cations can also be prepared.

2. By protonation.

By allowing the alkenes to protonation we can prepare the carbo cations as shown below.

$$CH_3-CH=CH_2 \xrightarrow[SO_2]{liquid} CH_3-CH^+-CH_3$$



$$CH_3-\overset{\overset{O}{||}}{C}-C_6H_5 + H^+ \longrightarrow CH_3-\overset{\overset{OH}{|}}{C^+}-C_6H_5$$

+

$$C_6H_5\,C \equiv\equiv N + H^+ \longrightarrow C_6H_5\,C^+ \equiv\equiv NH$$

Other methods.

$$CH_3Cl + AlCl_3 \longrightarrow CH_3^+ + AlCl_4^-$$

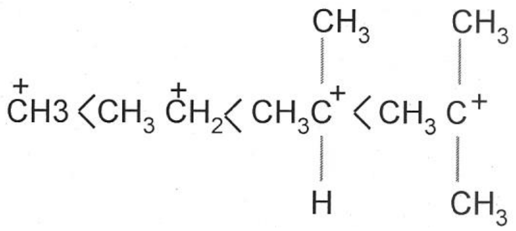
$$CH_3\,CO\,Cl + AlCl_3 \longrightarrow CH_3CO^+ + AlCl_4^-$$

$$C_6H_5CH_2\,Cl + AlCl_3 \longrightarrow C_6H_5\,CH_2^+ + AlCl4^-$$

Stability of carbo cations.

Being ionic carbo cations can't exist separately and so the stability is normally low. But it was found that some carbo cations are unstable and some others are more stable to a separable extent.

The stability of methyl, ethyl, iso propyl and tertiary butyl carbo cations are in the following increasing order.



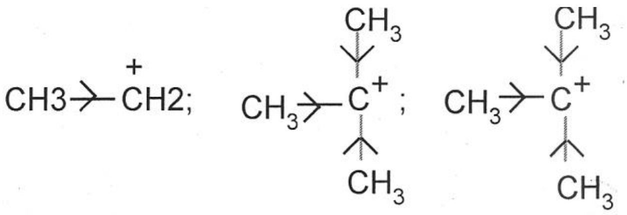
$$\overset{+}{C}H3 < CH_3\overset{+}{C}H_2 < CH_3\overset{+}{C}(CH_3)H < CH_3\overset{+}{C}(CH_3)CH_3$$

Generally inductive effect, resonance or mesomerism and hyper conjugation play an important role in deciding the stability of carbo cations as detailed below.

Inductive effect .

We know that methyl group has +I effect and supplies electrons to the carbon skeleton. This effect neutralises the +ve charge on the carbon atom and as result of this the stability of carbo cation increases.

In methyl carbo cation there is no methyl group, in ethyl group there are two, in iso propyl there are three and in tertiary butyl there are four methyl groups. Thus when we pass from the left to the right number of methyl groups goes on increasing and the neutralisatin effect also increased remarkably as depicted below.



$$CH3 \rightarrow \overset{+}{C}H2; \quad CH_3 \rightarrow C^+(CH_3)(CH_3); \quad CH_3 \rightarrow C^+(CH_3)(CH_3)$$

As a result methyl cation is least stable and tertiary butyl is the most stable one.

Hyper conjugation.

It is explained by taking ethly carbo cations as the example.

H H

H C CH_2 H C CH_2

H H

H H

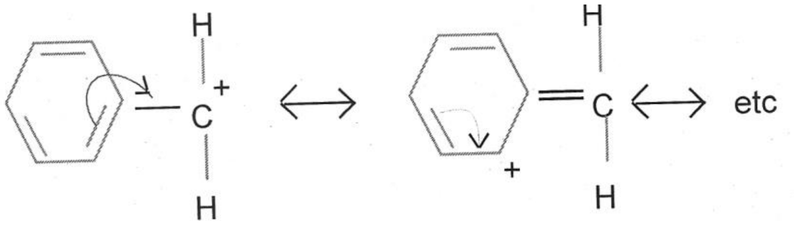
H C CH_2 H C CH_2

H H

Three structures are obtained for ethyl cation. In a similar way we will have seven forms and for tertiary butyl, ten canonical forms of hyper conjugation. This supports the order of stability given above.

Resonance .

Stabilisation of carbo cation by resonance can be explained by taking phenyl methyl cation as follows.



In a similar way the other canonical form of resonance can be drawn.

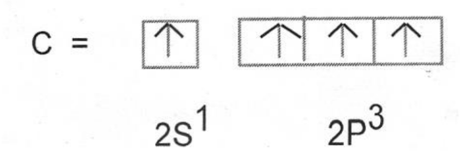
For phenyl methyl cation we will get three forms but for di phenyl methyl cation, seven forms and for tri phenyl methyl cation we will get a total of ten canonical forms. This shows that tri phenyl methyl cation is the most stable.

If we compare tertiary butyl carbo cation and tri phenyl methyl carbo cation, tri phenyl methyl carbo cation is the most stable.

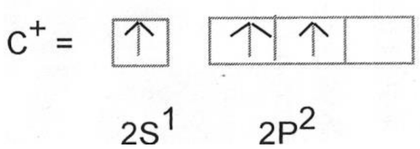
It is because for inductive effect and hyper conjugation, methyl group uses only the sigma bonds which are tightly held. But in tri phenyl methyl cation for resonance the phenyl group uses the more labile pi - electrons which are loosely held.

Structure of carbo cation .

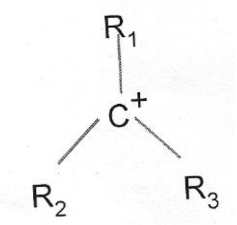
The box type valence shell electronic configuration of carbon in the exited state can be represented as follows.



But we know that in the formation of a carbo cation only the valence shell electron is removed. As a result the valence shell electronic configuration of the carbon atom in the carbo cation will be as follows.



There fore in c+ ion only sp2 hybridisation is possible. This hybridisation gives a trigonal planar structure to the carbo cations as shown below.



Where R can be hydrogen, methyl of phenyl group. Carbo cations are electro philic species and makes an electrophilic attack on the substrates.

CARBANION :

An organic species in which the central carbon atom has a loan pair of electrons in its valence shell is called the carbanion.

e.g.

CH_3^- ; $CH_3\,CH_2^-$ Ph_3C^-

Since the carbanion has a lone pair of electrons, they act as a very good nucleophilic reagent or a Lewis acid.

CLASSIFICATION :

Carbanions are classified in to the following three types.

1. Primary carbanion.

If the carbon atom carrying the negative charge is not bonded to any other carbon atom or to only one carbon atom directly, then it is called the primary carbanion.

e.g.

CH_3- ; CH_3CH_2- ; $(CH_3)3CCH_2$-

2. Secondary carbanion .

If the carbon atom carrying the -ve charge is attached directly two other carbon atoms, then it is called the secondary carbanion.

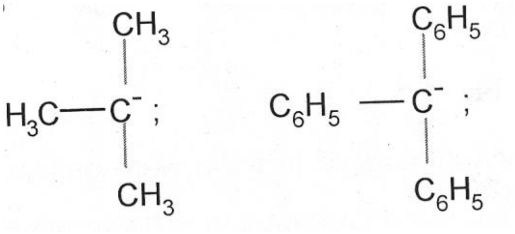
e.g.

$(CH_3)2CH$- ; (C6H5)2CH-

3. Tertiary carbanion .

If the carbon atom carrying the -ve charge is attached to three more carbon atoms directly then it is called the tertiary carbanion.

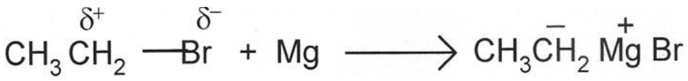
e.g.



$H_3C-\overset{CH_3}{\underset{CH_3}{C^-}}$; $C_6H_5-\overset{C_6H_5}{\underset{C_6H_5}{C^-}}$;

Generation of carbanions .

Though it is not a full fledged carbanion, Grignard reagent is a good example for carbanion which generates a full fledged carbanion during a chemical reactions as shown below.



$$\overset{\delta+}{CH_3CH_2}-\overset{\delta-}{Br} + Mg \longrightarrow CH_3\overset{-}{CH_2}\overset{+}{Mg}Br$$

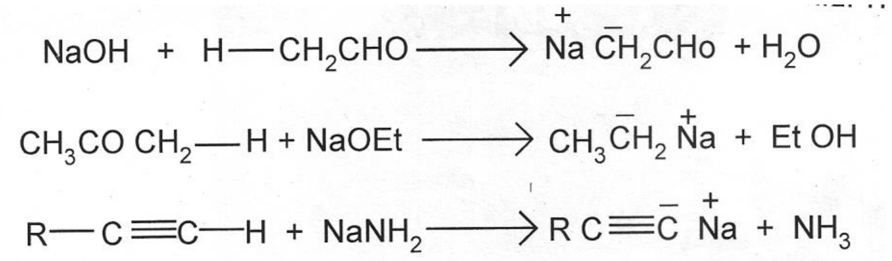
Similarly sodamide in ammonia solution reacts with acetylene to give sodium acetylide as given below which is a good example for a carbanion.

$$H-C\equiv C-H + \overset{+}{Na}\overset{-}{N}H2 \longrightarrow H-C\equiv\overset{-}{C}\quad\overset{+}{Na} + NH3$$

By de protonation.

When an organic compound having active methyl or methylene group is allowed to react with a strong base, de protonation takes place to give a carbanion as shown below.

e.g.



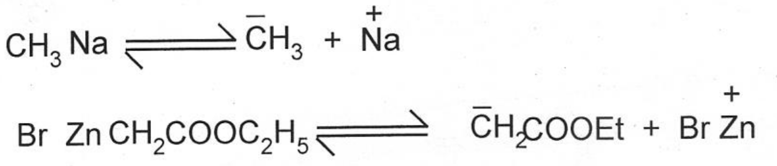
$$NaOH + H{-}CH_2CHO \longrightarrow \overset{+}{Na}\,\overset{-}{C}H_2CHo + H_2O$$

$$CH_3CO\,CH_2{-}H + NaOEt \longrightarrow CH_3\overset{-}{C}H_2\,\overset{+}{Na} + Et\,OH$$

$$R{-}C\equiv C{-}H + NaNH_2 \longrightarrow R\,C\equiv\overset{-}{C}\,\overset{+}{Na} + NH_3$$

By breaking a carbon - metal bond .

Metal alkylides undergo dissociation to give carbanions as shown below.

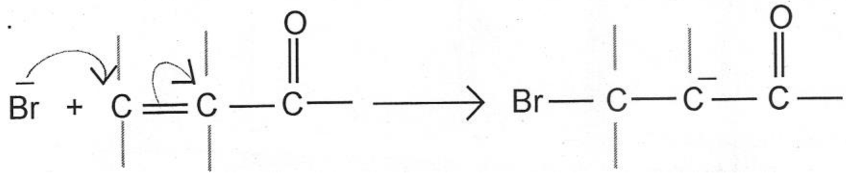


$$CH_3\,Na \rightleftharpoons \overset{-}{C}H_3 + \overset{+}{Na}$$

$$Br\,Zn\,CH_2COOC_2H_5 \rightleftharpoons \overset{-}{C}H_2COOEt + Br\,\overset{+}{Zn}$$

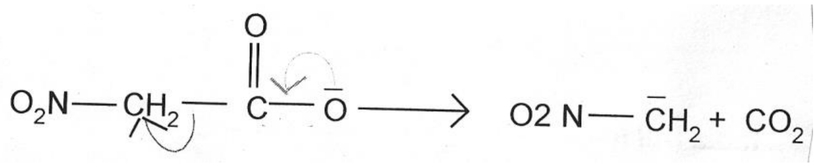
By the addition of a negative ion to an alkenic bond .

For example a bromide ion reacts as follows to give a carbanion.



By de carboxylation .

When carboxylate ions are subjected to decarboxylation, we get carbanion.



Stability of carbanions.

The stability of carbanions are determined by the following four factors namely,

1. Field effect or inductive effect,

2. Resonance,

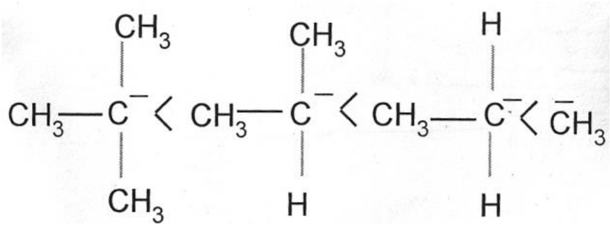
3. Aromatisation and

4. s - character.

which can be explained one by one.

1. Field effect or inductive effect.

The order of stability of primary, secondary and tertiary carbanions are in the following increasing order.



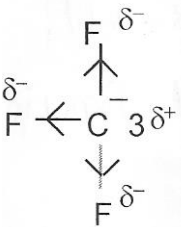
That is the methyl carbanion is the most stable and the tertiary carbanion is the least stable one.

It is because normally the + I groups - to the carbon carry ing the -ve charge, increases the -ve charge on it further, thus by decreasing the stability of carbanion. There fore if the increase in the number of methyl groups results in the decrease of stability of carbanions.

Therefore the tertiary butyl carbanion which has three methyl groups is the least stable and the methyl carbanion which has no methyl group is the most stable. Thus the stability of carbanions can be represented in the increasing order as follows.

tertiary secondary primary methyl carbanion.

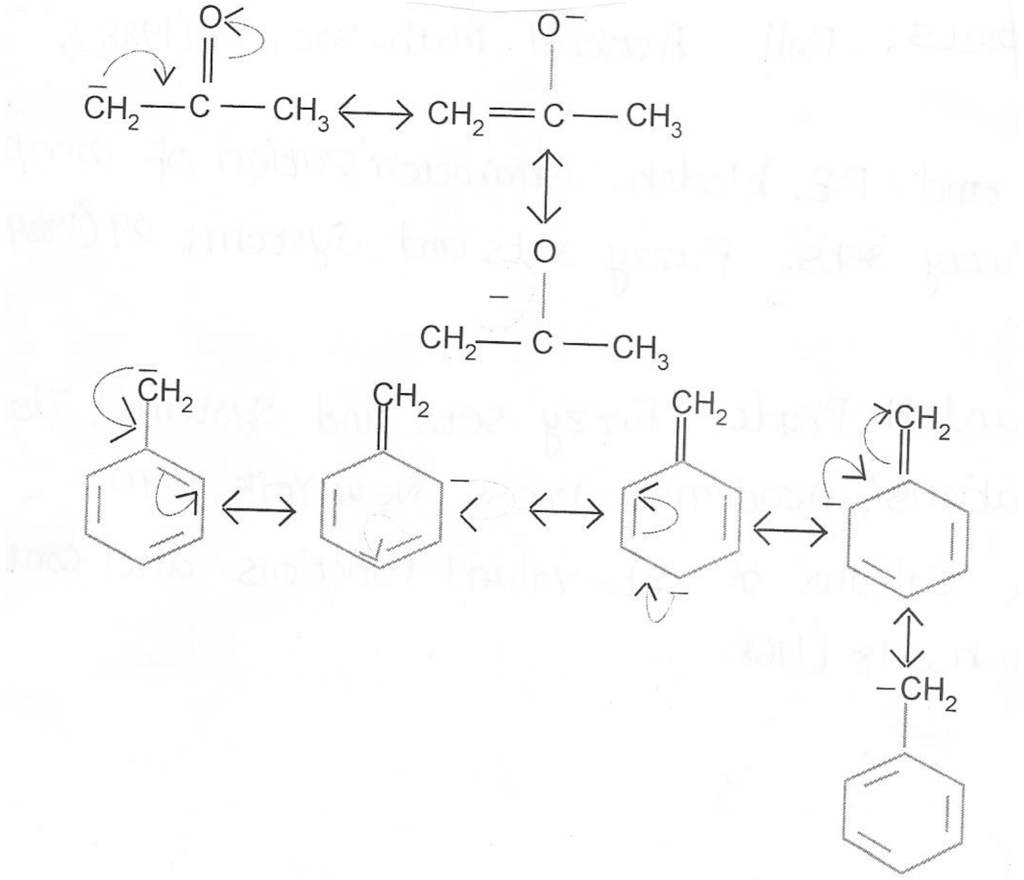
But on the other hand, groups with -I effect attached to the carbanion, increase their stability. To explain this, let us take the following carbanion as our examples.



Here the fluorine atom having a strong -I effect, attracts the electron density on the carbanion thus by making it more stable. Therefore, more the number of -I groups, more the stability of the carbanions.

Resonance effect.

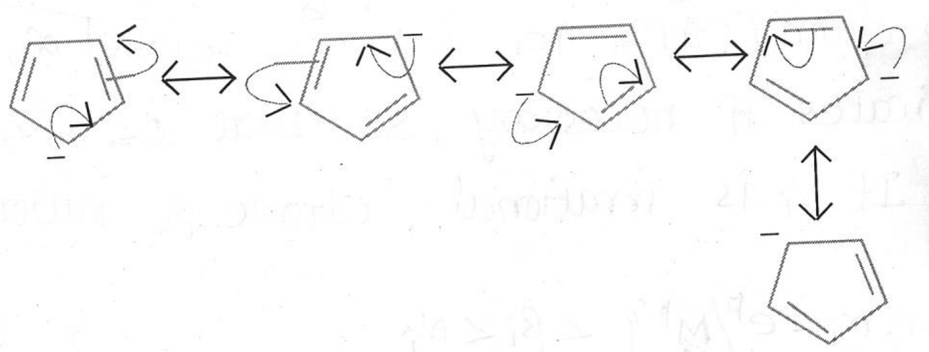
If a double bond or a phenyl group is present in the position to the carbanion then resonance takes place as shown below.



These resonance effects decreases the electron density on the carbanion, which is distributed in side the benzene ring. As a result the carbanion gets stabilised.

Aromatisation.

In certain cyclic compounds where the -ve carbon ion is present in a ring with a conjugated pi - electron system, then this loan pair of electrons undergo delocalisation, to fulfill the (4n + 2) pi - electron rule in order to attain aromaticity. Such carbanions are more stable. This fact can be explained by taking cyclo penta dienyl anion.



Thus it is clear that the property of aromatisation also helps stabilising the carbanions.

s - character.

The s - character of the - carbon to the carbon carrying the

-ve charge also play an important role in deciding the stability of the carbanions. The decreasing order of the stabilities of the following carbanions can be explained on the basis of the said principle.

CH C CH

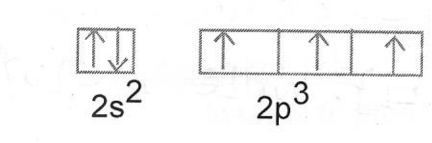
The reason is that, in the ethynide ion the - carbon atom is sp - hybridised which has 50% s - character. But in the ethenide ion the - carbon is sp^2 hybridised where the carbon atom has 33.33% s - character. On the other hand in the ethanide ion the - carbon is sp^3 - hybridised in which the carbon atom has only 25% of s - character.

There fore sp - carbon attracts the electronic charge on the carbanion more effectively and nullyfied the -ve charge thus by making it the most stable . When we pass from the left to the right the s - character goes on decreasing and so their electronegativity also decreases, thus by decreasing the stability.

More over in ethanide ion the - methyl group present with its +I effect also destabilises it. Thus the ethanide ion is the least stable and the ethynide ion is the most stable.

STRUCTURE OF CARBANION:

The exited state valence shell electronic configuration of carbon atom in a carbanion can be represented as follows.



So the carbon atom carrying the -ve charge is sp^3 hybridised. Thus a carbanion must have a tetra hedral geometry in which the carbon atom is at the centre of th tetra hedran, the three H - atoms are pointing towards ht e three corners of the tetrahedran and the lone pair of electrons is pointing towards the fourth corner of the tetrahedran as drawn below.

C

H

H

H

structure of carbanion

Carbanions are nucleo philic agents and so makes a nucleo philic attack on the substrate during chemical reactions. Carbanions under go umbrella inversion similar to that of ammonia.

FREE RADICALS :

A neutral species, having atleast one unpaired electron in its valence shell with higher energy than that in the ground state, is called the free radical.

e.g.

Cl = chlorine free radical

= methyl free radical

Ph_3COO = benzoyl oxy free radical.

Types of free radical .

Free radical are classified in to two groups on the basis of their stability as follows.

One type of free radical is called stable or the long lived free radicals which has a long live.

e.g.

Ph_3 COO

The other type of free radical is called the transient or short lived free radicals.

e.g.

Ph, Ph COO

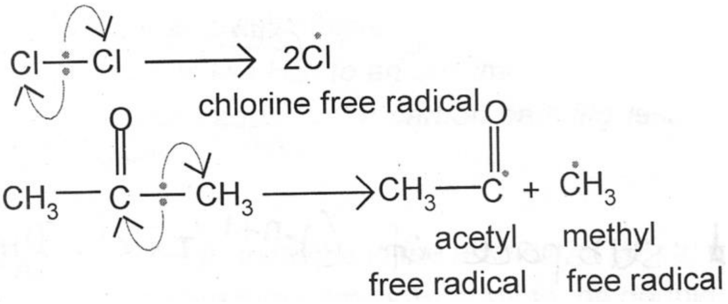
Energy of free radical .

We know that sodium meatal and the hydrogen atom have and unpaired electron in their valence shells. But they are in the ground state and hence they can't act as free radicals. There fore a free radical must be in the higher energy state so that it can act as a reactive intermediate.

Generation of free radicals.

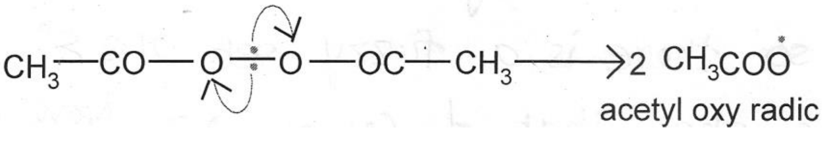
1. By photo chemical reactions.

In presence of sun light and high temperature, homo lytic fission takes place to give free radicals as shown below.



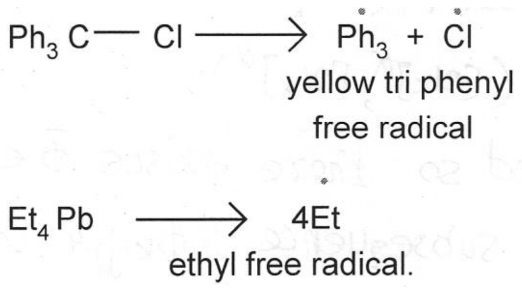
Thermal generation .

Acyl peroxides in vapour phase at high temperature yield free radicals as follows.



Chemical method .

Alkyl and aryl metals liberate free radicals according to the following reactions .

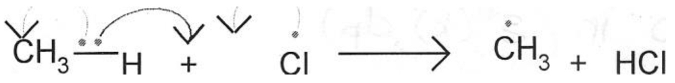


yellow tri phenyl free radical

ethyl free radical.

From other free radicals .

For example when methane is allowed to react with chlorine free radical, we get methyl free radical as shown below.

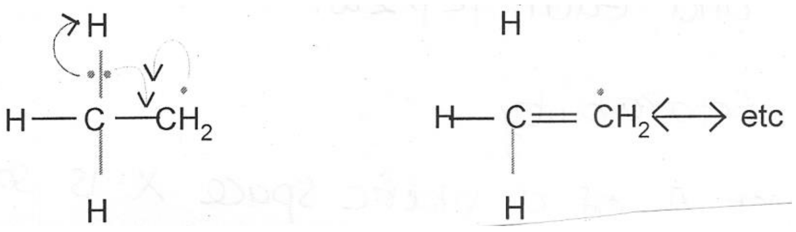


STABILITY OF FREE RADICALS :

Like carbo cations, the stability of free radicals are also in the increasing order as follows.

primary secondary tertiary

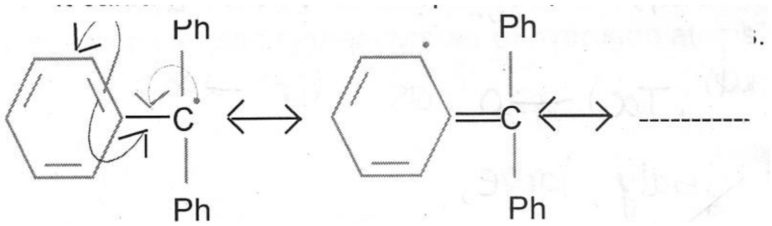
This fact can be explained as follows. A primary free radical under goes resonance as follows.



Similarly we can have two more canonical forms for the other two methyl hydrogen atoms also which increases the stability.

But in a secondary free radical we will get six canonical forms and in the tertiary free radicals there will be nine canonical forms for nine hydrogen atoms present. As a result the tertiary free radical is the most stable and the primary free radical is least stable.

In a similar way benzene nucleus also stabilises the free radicals due to resonance as shown below.

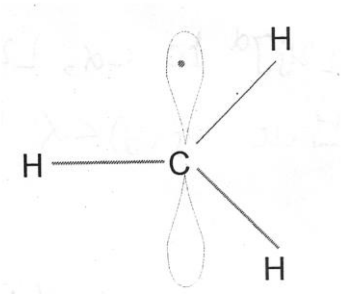


In a similar way three more canonical forms can also been drawn for a phenyl group and for each phenyl group we will get three canonical forms. Hence it is clear that the tertiary free radical is the most stable and the primary free radical is the least stable.

STRUCTURE OF FREE RADICALS :

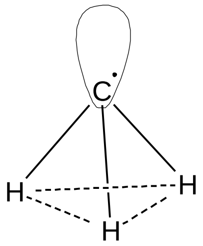
Since there can be one or more unpaired electrons in a free radical, they are para magnetic in nature even though it is electrically neutral. It is highly reactive, since the unpaired electron is badly in need of another electron to get paired in order to attain stability.

The central carbon atom of the free radical is believed to have sp^2 hybridisation leaving one p - orbital free of hybridisation. As a result of this, free radicals have a planar structure as shown below.



Since it is planar, during chemical reactions, there is possibility of attack on both sides by the attacking reagent and so we will get a racemic product.

Another school of thought says that the central carbon atom, if the free radical is sp^3 hybridised it will have pyramidal structur with the unpaired electron in one of the hybridised orbitals as shown below.



Since the pyramidal shaped free radical can be chiral if the three groups attached are different, we may expect products with retention of configuration. It is because the attacking reagent can approach the free radical through one direction only.

Free radicals also under go umbrella inversion as that in ammonia.

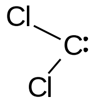
CARBENES :

A neutral intermediate in which the carbon atom has only two valencies is called a carbene.

e.g.

carbene = $CH_2\colon$

di chloro carbene =



As for as the carbenes are concerned there is no possibility of having a tertiary carbene because the carbon in carbene is bi valent. There fore the carbene is also called the methylene.

GENERATION :

They are obtained by the photo chemical or thermal decomposition of diazo alkanes.

R CH N N [RCH] + N_2

diazo compound

N N CHCOOEt [CHCOOEt] + N_2

diazo compound

C O + CO

Ketene

Similarly when chloroform is allowed to react with a base dichloro carbene is obtained as follows.

$$CHCl_3 \xrightarrow[H_2O]{OH^-} Cl_2C\text{—}Cl \longrightarrow CCl_2$$

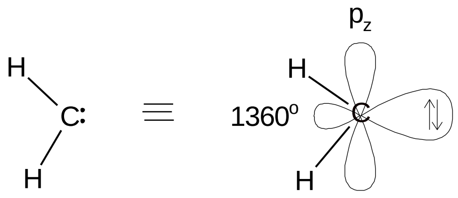
dichloro carbene

Carbene obtained from diazo compound was found to be more active than that obtained from ketene.

Structure of carbene.

The two non bonded electrons on the carbon may be in a singlet state (paired) or in a triplet state (unpaired).

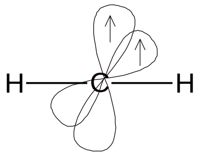
The singlet carbene is believed to have sp_2 hybridised with a bent structure having a bond angle equal to 136º. Out of these three hybridised orbitals two are used for bond formation and in the third orbital the two electrons placed in paired state. The structure of a singlet carbene can be schematically represented as follows.



singlet structure

In the singlet carbene the p_Z orbital is vacant. Hence it is ready to accept electrons. As a result this species act as an electrophilic reagent.

But as for as the triplet carbene is considered the central carbon atom is believed to be sp - hybridised with linear structure. The two sp - orbitals hold two hydrogen atoms and the two unhybridised p - orbitals carry the two unpaired electrons, each one as shown below.



In this triplet state there are two unpaired electrons in two p - orbitals. There fore this species is a di radical which can act as a free radical in chemical reactions.

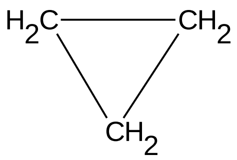
CYCLO ALKANES :

Cyclo alkanes also called cyclo paraffins are saturated hydrocarbons in which a number of methylene groups are joined by single covalent bonds to form a ring. Since they contain number of methylene groups they are called poly methylenes. They are also known as Alicyclic compounds meaning aliphatic cyclic, because their properties are similar to those of aliphatic hydrocarbons.

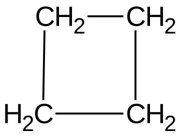
The unsubstituted cycloalkanes form a homologous series with a general molecular formula C_nH_{2n} where 'n' is the number of carbon atoms in the molecule. This general formula same as that for the alkenes but saturated. The first member has the value of 'n' equal to three and its name is cyclopropane.

Symbols (or) Method of representing cyclo alkanes.

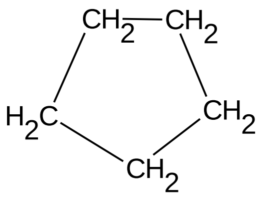
Normally cyclo alkanes are represented in the form of polygons with groups at the corners of the polygon. For example cyclopropane is represented as a triangle, cyclobutane as a square and so on with the sufficient number of methylene groups as represented below.



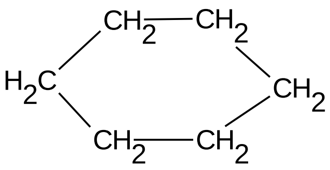
Cyclo propane



Cyclobutane



Cyclo pentane

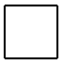


Cyclohexane

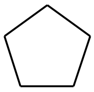
Condensed symbols.

For convenience and simplicity, aliphatic rings are often represented by simple geometric figures. That is cyclo propane is represented by a triangle, cyclo butane by a square and so on as shown below.

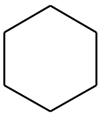
Cyclo propane



Cyclo butane



Cyclo pentane



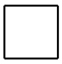
Cyclo hexane

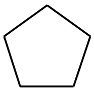
NOMENCLATURE :

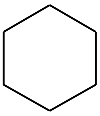
1. They are named similar to that of alkanes. The name of the unsubstituted cyclo alkane is derived just by prefixing the word 'cyclo' to the

name of the corresponding normal alkane having the same number of carbon atoms.


Cyclo propane

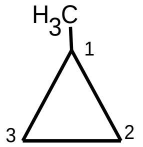

Cyclo butane

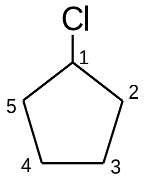

Cyclo pentane

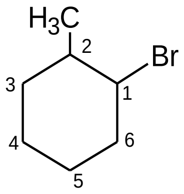

Cyclo hexane

The substituents on the ring should be numbered in such a way that, they get the lowest number possible and then named along with the position number.

e.g.


Methyl Cyclo propane


Chloro cyclopentane

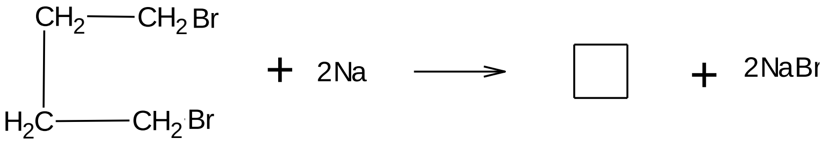

1 - bromo - 2 - methyl cyclo hexane

PREPARATION OF CYCLO ALKANES :

1. By Wurtz reaction .

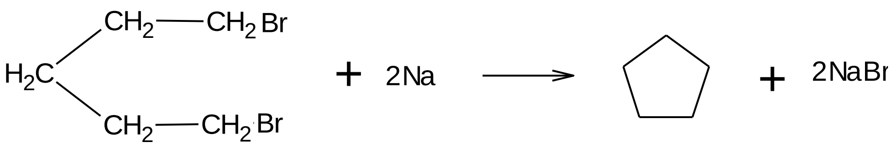
Normally wurtz reaction is designed to prepare a higher alkane from the lower alkyl halides in presence of sodium of zinc. It is also used to prepare cyclo alkanes.

When 1,3 - to 1,6 - dibromo alkanes are allowed to react with metallic sodium or zinc, we get cyclo alkanes as shown below.



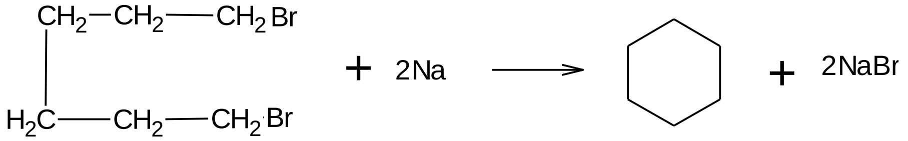
Tetramethylene bromide

Cyclobutane



Pentamethylene bromide

Cyclopentane



Hexamethylene bromide

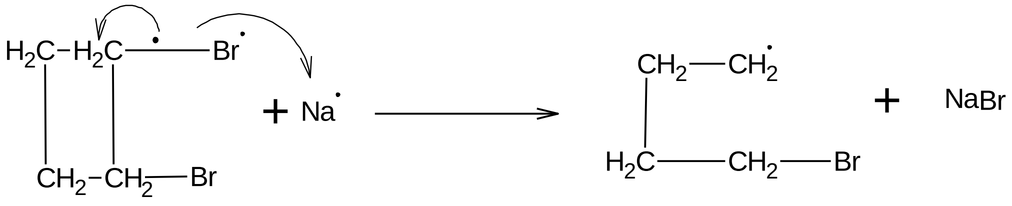
Cyclohexane

Mechanism of the reaction.

Wurtz reaction is believed to follow both the free radical and ionic mechanism as detailed below.

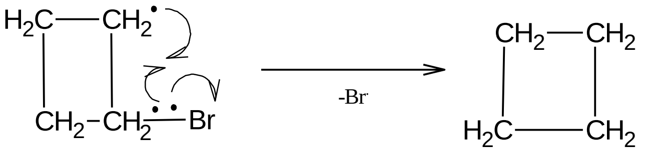
Free radical mechanism.

In the first of step of the free radical mechanism, metallic sodium reacts with dibromo alkane to give an alkyl free radical.



Free radical

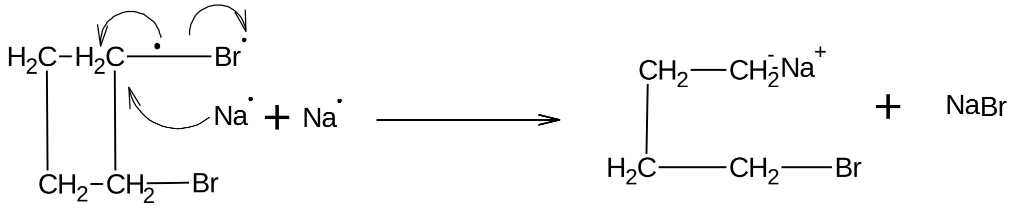
Then in the second step, the free radical formed under goes internal cyclisation as shown below to give the corresponding cyclo alkane.



Cyclobutane

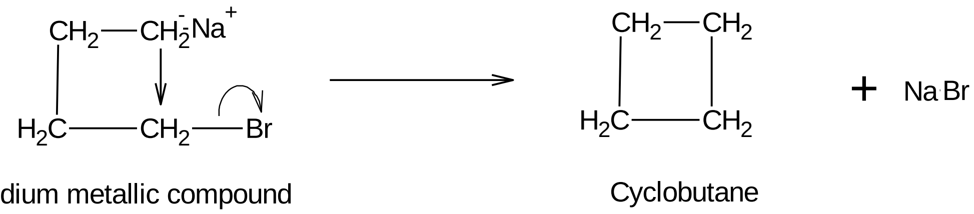
Ionic mechanism .

In the first step of ionic mechanism, two atoms of sodium react with dibromo alkane to give an organo metallic compound.



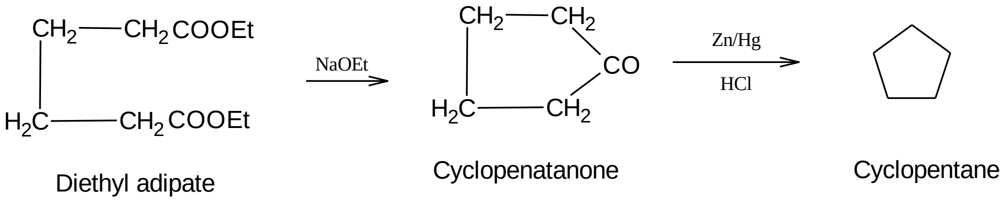
Organo metallic compound

Then in the second step the organo metallic compound releases a molecule of NaBr and under goes cyclisation to give cyclo butane as shown below.



By DIECKMANN ring closure reaction .

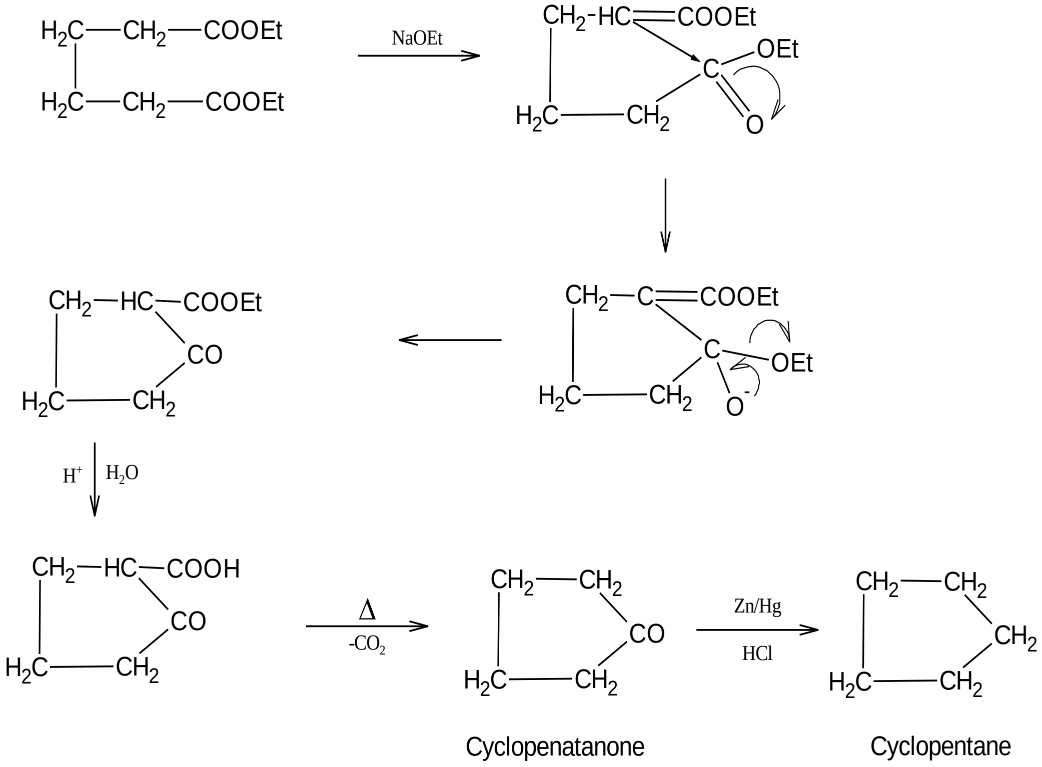
When diethyl esters of poly methylene dicarboxylic acids are allowed to react with sodium ethoxide we get cyclic ketones. These cyclic ketones when subjected to Clemenson reduction we get cycloalkanes.



Mechanism this reaction .

This reaction is actually an extension of intramolecular Claison condensation which give cyclic ketones.

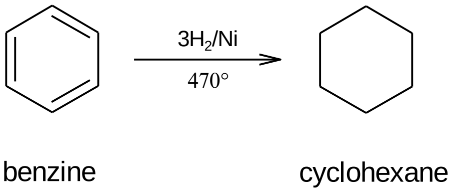
The various steps involved in this reaction can be explained as detailed as below.



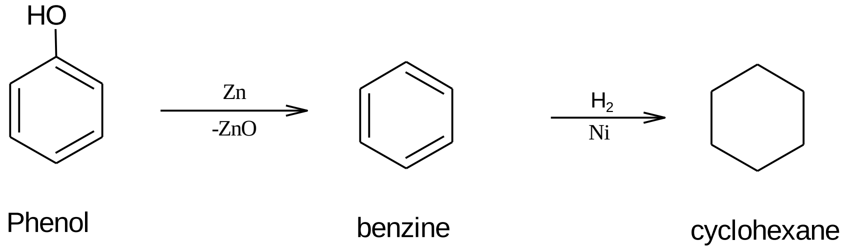
Similarly cyclohexane and other cycloalkanes can be prepared by using this method.

By reduction of aromatic compounds .

When benzene is reduced by hydrogen in presence of Ni at 470^{o} we get cyclohexane as shown below.



From phenol we can get cyclohexane by distilling it with Zn dust followed by reduction in presence of Nickel.



BAYER’S STRAIN THEORY : (Stability of cycloalkanes)

The cycloalkanes are classified in to three groups depending on their size as follows.

Cyclopropane and cyclobutane are placed under small rings, five sex and seven membered rings are called the medium rings and the cyclo octane and higher members are placed under bigger group.

Among these, the small rings have very low stability, so that they under go addition reactions like alkenes.

But the medium rings namely cyclopentane, cyclohexane and cycloheptane are very stable and participated only in substitution reactions like normal alkanes.

To account for this variation in stability of cycloalkanes Bayer introduced his concept called Bayer’s strain theory.

This theory states that ‘in cyclo alkanes the valence bond angle of tetrahedral geometry is altered from its standard value of 109°28’ and a strain developed due to this is responsible for this anomaly in stability ‘. Bayer found that, more the deviation from the normal tetrahedral angle, the greater is the strain and lesser is the stability of cyclo alkane.

Assuming all the rings to be planar and since the total strain is shared by two bonds, he calculated the bond angle strain of various rings as follow.

Cycloalkane	Amount of strain.
Cclopropane	$\frac{1}{2}\left(109^{\circ}28'-60^{\circ}\right)=+24^{\circ}44'$
Cyclobutane	$\frac{1}{2}\left(109^{\circ}28'-90^{\circ}\right)=+9^{\circ}44'$
Cyclopentane	$\frac{1}{2}\left(109^{\circ}28'-108^{\circ}\right)=+0^{\circ}44'$

Cyclohexane $\frac{1}{2}\left(109^\circ 28' - 120^\circ\right) = -5^\circ 16'$

Cycloheptane $\frac{1}{2}\left(109^\circ 28' - 128^\circ 34'\right) = -9^\circ 33'$

From the above calculations it is seen that after ignoring sign the bond angle strain goes on increasing from cyclopropane to cyclopentane and then increases afterwards.

Therefore according to Bayer's strain theory, the stability must increases from cylopropane to cyclopentane and there after decrease from cyclohexane.

Limitations of Bayer's theory.

According to this, we see that cyclohexane must be less stable than cyclopentane which is not true. Cyclohexane is even more stable than cyclopentane. Thus this theory well explains in the case of small rings but fails in cyclohexane and in higher rings.

Therefore a modification was needed and was given by Coulson.

Coulson's modification.

Bayer's theory failed in higher rings because it was based on the assumption that all the rings are planar irrespective of the size.

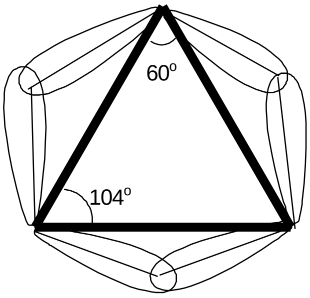
Secondly the strain was calculated on the base that the tetrahedral angle must be 109^{o} 28'.

But physical measurements have proved that except cyclopropane the other rings can not be planar.

Coulson showed that the smallest tetrahedral angle that can be possible is 104o. Therefore as per Coulson's modification the bond angle strains in cyclopropane and cyclobutane can be calculated as follows.

Compound	Bond angle deviation
Cyclopropane	$\frac{140^\circ - 60^\circ}{2} = \frac{44^\circ}{2} = 22^\circ$
Cyclobutane	$\frac{140^\circ - 90^\circ}{2} = \frac{14^\circ}{2} = 7^\circ$

Coulson explained that in cyclopropane due to this deviation in bond angle the orbitals are not pointing towards one another in same line which doesn't allow effective overlap as shown below.



But in cyclobutane, though it has bent bonds the loss of overlap is lesser since bond angle deviation in only 7°, when compared to cyclopropane where the bond angle deviation is 22°.

Thus due to this ineffective overlap, the bonds are very weak in cyclopropane and hence they are easily broken. As a result cyclo propane undergoes addition reactions just like unsaturated compounds.

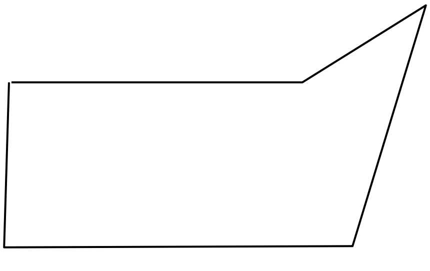
But we move up the series the bond angle deviations goes on decreasing and hence stability goes on increasing and so they undergo substitution reactions like saturated compounds.

SACHSE - MOHR CONCEPT OF STRAINLESS RINGS :

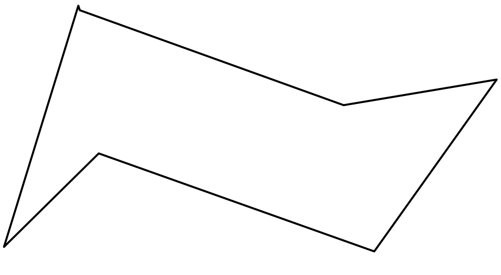
Sachse and Mohr stated that cyclopropane and cyclobutane have planar structures whereas cyclopentane and higher rings must exist in puckered form, that is not having planar structures.

Therefore cyclopentane and cyclohexane molecules are able to relax the strain in them. Hence they are stabler molecules.

The puckered forms of cyclopentane and cyclohexane can be drawn as shown below.



Cyclopentane



Cyclohexane

ELECTROPHILIC and FREE RADICAL ADDITION IN ALKENES :

Addition reactions.

Addition reaction is one in which a bond is broken and two sigma bonds are formed on the carbon atoms carrying the double bond.

e.g.

$$CH_2 = CH_2 + H_2 \longrightarrow CH_3 - CH_3$$

Ethylene Ethane

$$CH \equiv CH + H_2 \longrightarrow CH_2 = CH_2$$

Acetylene Ethylene

$$CH_2 = CH_2 + Br_2 \longrightarrow CH_2Br - CH_2Br$$

Ethylene bromide

$$CH_2 = CH_2 + HBr \longrightarrow CH_3 - CH_2Br$$

Ethylbromide

$$CH_2 = CH_2 + HOCl \longrightarrow CH_2OH - CH_2Cl$$

Ethylenechlorohydrin

$$CH_2 = CH_2 + H^+HSO_4 \xrightarrow{H_2SO_4} CH_3 - CH_2HSO_4$$

Ethyl hydrogen sulphate

$$CH_2 = CH_2 + HOH \xrightarrow{H_2O} CH_3 - CH_2OH$$

Ethyl alcohol

The addition reactions have very much analytical and commercial utility. For example the bromination reaction is useful in determining and estimating the double bonds.

1,2 - Addition reactions.

The addition reaction in which the two parts of the addendum add to the adjacent carbon atoms is called the 1,2 - addition reaction which is as given below.

e.g.

$$\underset{\text{Propene}}{CH_3CH = CH_2} + H_2 \xrightarrow{Ni} \underset{\text{Propane}}{CH_3\ CH_2\ CH_3}$$

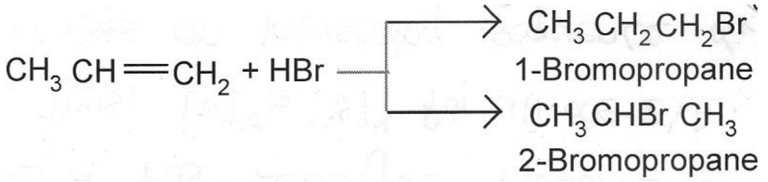
Addition of HX (Hydrogen halides) to symmetrical alkenes .

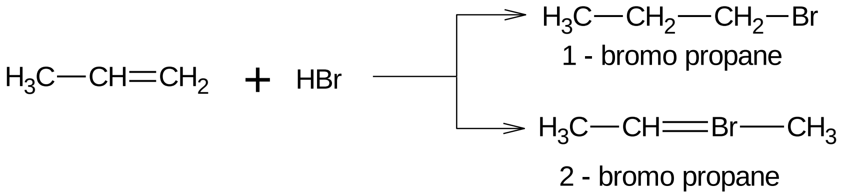
Hydrogen halides for example HBr adds to symmetrical alkenes like ethylene as follows.

$$\underset{\text{Ethylene}}{CH_2 = CH_2} + HBr \longrightarrow \underset{\text{Ethylbromide}}{CH_3 - CH_2Br}$$

Addition of HX to unsymmetrical alkenes .

But in the case unsymmetrical alkenes like propene the addendum for example HBr may add in two different ways to give two different products as follows.





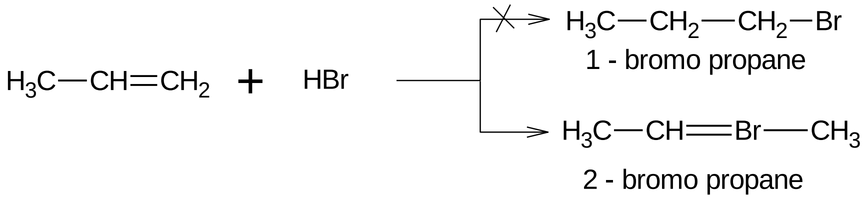
But in this addition reaction 2-bromopropane alone is formed.

Markownikoff rule :

In order to predict the product obtained in the addition of HBr to an unsymmetrical olefins Markownikoff formulated a rule called the Markownikoff's rule which states that " *in the addition of an addendum like HBr to an unsymmetrical olefin, the -ve part of the addendum adds to the carbon carrying lesser number of carbon atoms*".

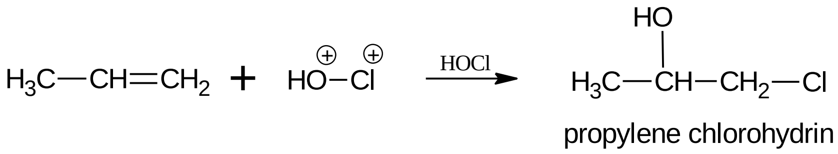
e.g.

For example in the addition of HBr to propene the -ve part of the addendum namely Br adds to the double bonded carbon which has lesser number of carbon atoms as shown below.



It can also be said that the positive part namely the H+, adds to the carbon carrying higher number of hydrogen atoms.

e.g. 2.

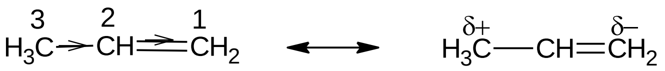


This reaction follows ionic mechanism. Moreover the reason for the formation of Markownikoff's product can be explained as follows.

1. Electron displacement effects.

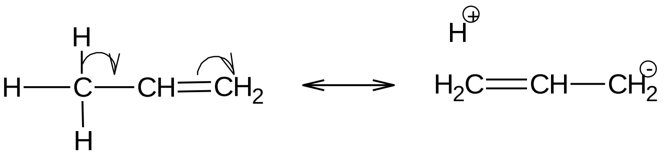
a). +I effect of methyl group.

The +I effect of methyl group makes the end carbon atom a partially -ve one as shown below.



b. Hyper conjugation effect.

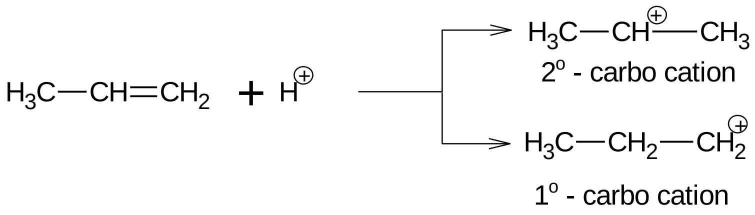
More over the methyl group attached to the sp^2 carbon undergoes hyper conjugation as shown below and makes the end carbon -ve.



These two electron displacement effects make the c1-carbon atom -ve, so that H adds to this atom and Br adds to the C2 atom.

2. The stability of carbo cation.

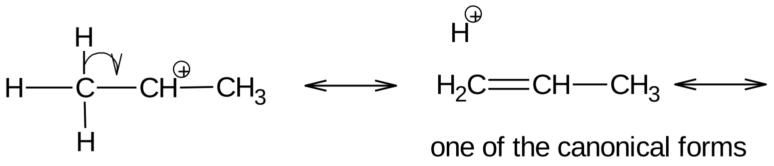
In the absence of these two electron displacement effects the H has equal chance to attack C1 or C2- atom as shown below to give two different carbo cations.



That is the attack by H on C1 - carbon gives a secondary carbo cation and on C2 - carbon gives a primary carbo cation .

We know that the carbo cations are sp2 hybridised and hence the methyl groups attached to them will undergo automatically hyper conjugation so as to give them stability.

In a secondary carbo cation there are two methyl groups which has a total of six - hydrogen atoms and so there will be six canonical forms as shown below.



Secondary carbo cation

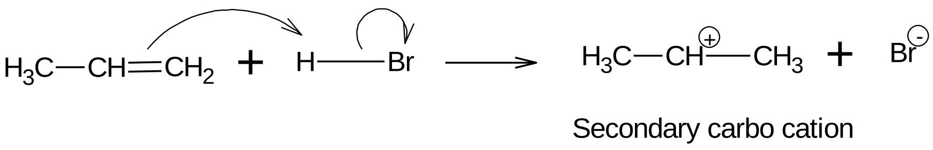
In a similar way we can have five more canonical forms for a secondary carbo cation.

But on the other hand for a primary carbo cation there is only one methyl group attached to cation with three - hydrogen atoms.

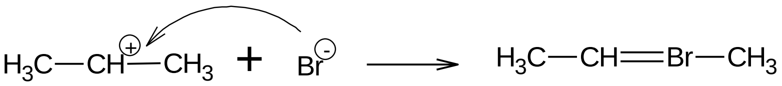
These three hydrogen atoms can give only three canonical forms on hyper conjugation.

Thus it is clear that only a secondary carbo cation will be produced because of its higher stability.

Therefore in the first step the +ve part namely H adds to the C1- atom to give the more stable carbo cation as shown below.



Then in the second step the -ve part of the addendum namely Br adds to the C2 carbon as shown below to give the said product.



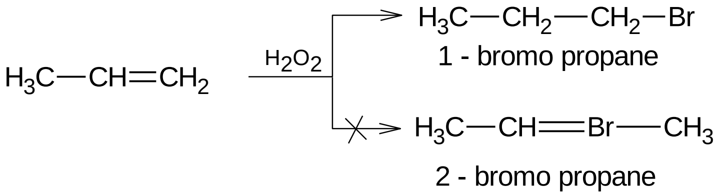
2 - bromopropane

This is the reason why the addition reaction takes place according to the Markownikoff's rule.

KHARASCH - PEROXIDE EFFECT or PEROXIDE EFFECT:

Anti Markownikoff addition or Free radical addition.

When HBr is allowed to undergo addition reaction with an unsymmetrical olefin like propene, in presence of peroxides or uv - light, it adds against Markownikoff's rule to give 1 - bromo propane as shown below and not 2 - bromo propane as in Markownikoff' addition.



This type of addition reaction which takes place in contrary to Markownikoff's rule is called the Kharasch - peroxide effect or simply the peroxide effect. It is also called anti Markownikoff's addition.

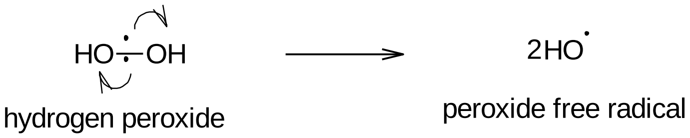
Mechanism.

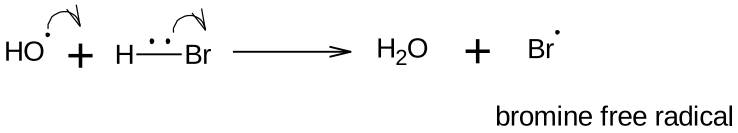
This reaction follows free radical mechanism . The various steps involved in this reaction can be explained as follows.

Step - 1, formation free radical.

In the first step in presence of a peroxide like H_2O_2 or benzoyl peroxide or in presence of uv - light HBr undergoes homolytic fission to give bromine and hydrogen free radicals as shown below.

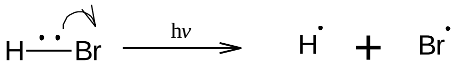
a). In presence of a peroxide.





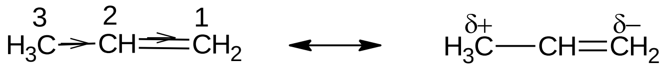
b). In presence of uv - light.

In presence of uv - light HBr itself dissociated to give bromine and hydrogen free radicals as given below.

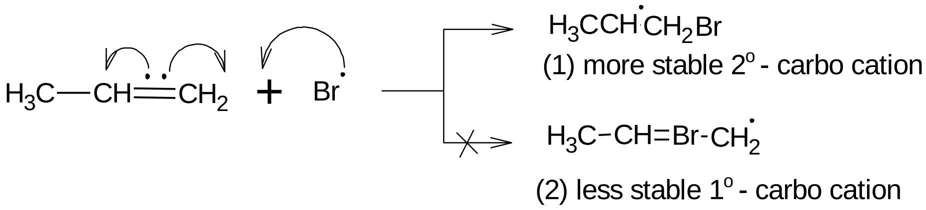


Step - 2, addition of bromine radical to propene.

The +I effect of methyl group attached to the double bonded carbon makes C1- partially -vely charged as shown below.



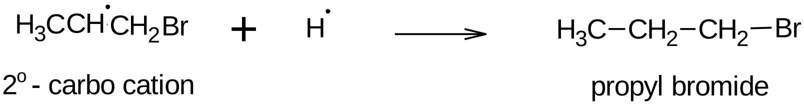
Now, out of hydrogen and bromine free radicals, bromine free radical being less stable and hence more reactive, adds first to the C1 - carbon of alkene as shown to give a more stable carbo cation.



Here the free radical (1) is formed because we know that a secondary free radical is the most stable one than the primary one.

Step - 3, formation of the product.

Finally the carbo cation (1) reacts with the hydrogen free radical to the product namely 1 - bromo propane as shown below.

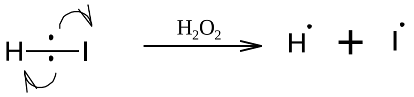


Special features.

But HF, HCl and HI doesn't give the anti Markownikoff's product even in the presence of peroxides.

The reason for this fact can be explained as follows. HF and HCl being more ionic in nature as compared to HBr, they don’t give free radicals even in presence of peroxides. Therefore they do not give free radical addition reactions.

On the other hand HI being more covalent than HBr, easily give hydrogen and iodine free radicals. But the iodine free radicals formed, being highly unstable, combine with another iodine free radical to give iodine molecule as soon as they are formed as shown below.



$$H:I \xrightarrow{H_2O_2} H^{\bullet} + I^{\bullet}$$

$$2I^{\bullet} \longrightarrow I_2$$

HYDROBORATION :

The addition of borane (BH_3) to alkenes to give trialkyl boranes is called the hydroboration reaction or hydroboration of alkenes.

e.g.

For example propylene undergoes addition with borane to tripropyl borane as follows.

$$3\,H_3C-CH=CH_2 \longrightarrow (H_3CCH_2CH_2)_3B$$

Propylene tri - propyl borane

Mechanism.

Borane is unstable even at ordinary temperature. So it dimerises to give a dimer as given below, which is a stable one and so doesn’t under go addition reaction.

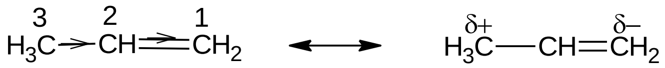
$$2\,BH_3 \longrightarrow H_2B-BH_2 + H_2\uparrow$$

Borane Propylene

But borane gives complexes with compounds like tetrahydrofuran (THF) and trialkyl amines (R_3N). In these complexes borane exists in the monomeric form. Therefore hydroboration can be done with borane at the moment of its liberation or using these complexes.

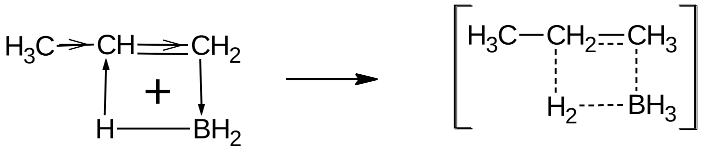
Hydroboration takes place against the Markownikoff’s rule. The mechanism of addition of borane to alkenes can be explained as follows.

The methyl group attached to the double bonded carbon, by its +I effect makes the C1- carbon partially -ve charged as shown below.



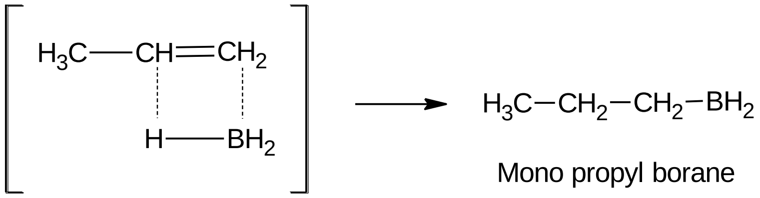
$$\overset{3}{H_3C}\rightarrow\overset{2}{CH}=\overset{1}{CH_2} \longleftrightarrow \overset{\delta+}{H_3C}-CH=\overset{\delta-}{CH_2}$$

Then in the first step, the electron deficient atom namely boran of borane adds to the alkene as shown below to give a four centered cyclic intermediate as follows.



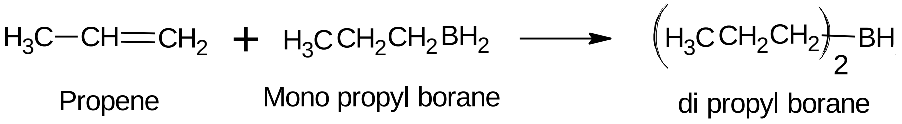
Four centered cyclic intermediate

Then the four centered cyclic intermediate rearranges the bonds to give the product as given below.

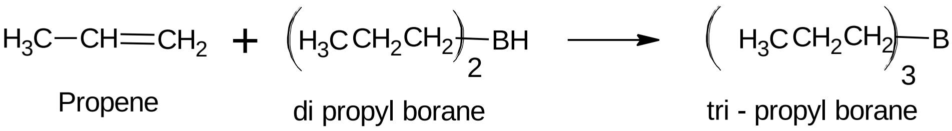


Four centered cyclic intermediate

The addition of borane to olefins is a cis addition. In a similar way mono alkyl borane adds to two more molecules of propene step wise to give di alkyl and trialkyl boranes as show below.



$$H_3C-CH=CH_2 + H_3CCH_2CH_2BH_2 \longrightarrow (H_3CCH_2CH_2)_2-BH$$

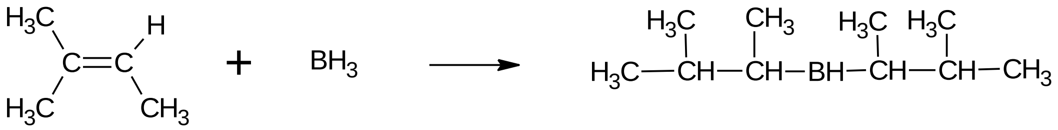


$$H_3C-CH=CH_2 + (H_3CCH_2CH_2)_2-BH \longrightarrow (H_3CCH_2CH_2)_3-B$$

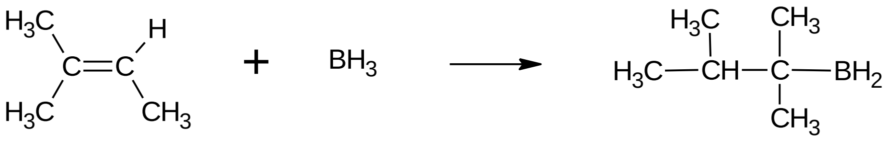
Special features.

If bulky groups are present in double bonded carbon atoms, then di- or mono- alkyl boranes are formed depending on the bulkiness of groups due to steric effect.

For example 2 - methyl butene gives di alkyl derivative where as 2,3 - methyl butane gives only mono alkyl boran as shown below.



di - symmetrical amyl borane

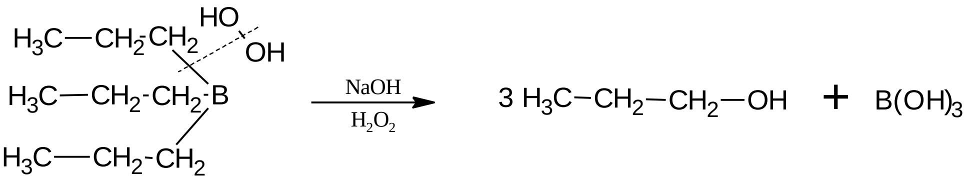


Thexyl borane

Applications.

The product obtained in the hydroboration reaction can be used for preparation of primary alcohols.

For example tri propyl borane obtained when subjected to hydrolysis in presence of hydrogen peroxide and sodium hydroxide we get propyl alcohol as shown below.

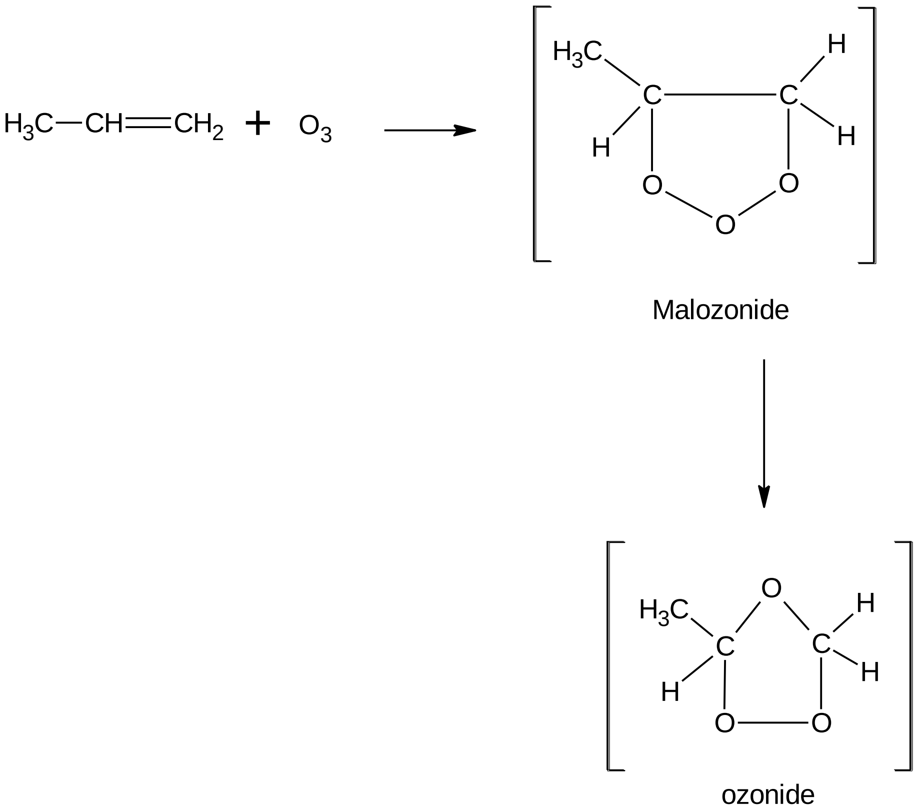


OZONOLYSIS (or) OZONIZATION:

The complete process of preparing ozonide, decomposing it and analising the products is called the ozonolysis.

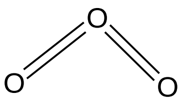
Alkenes dissolved in inert solvents like chloroform, carbon tetrachloride or glacial acetic acid when allowed to react with ozone at lower temperatures, addition takes place across the double bond to give first, an unstable intermediate called molozonide which spontaneously isomerises to give a stable compound namely ozonide.

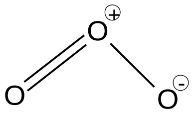
The overall reaction can be explained as follows taking propylene as an example.

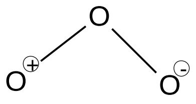


Mechanism of this reaction .

Ozone exists in the following resonating structures.

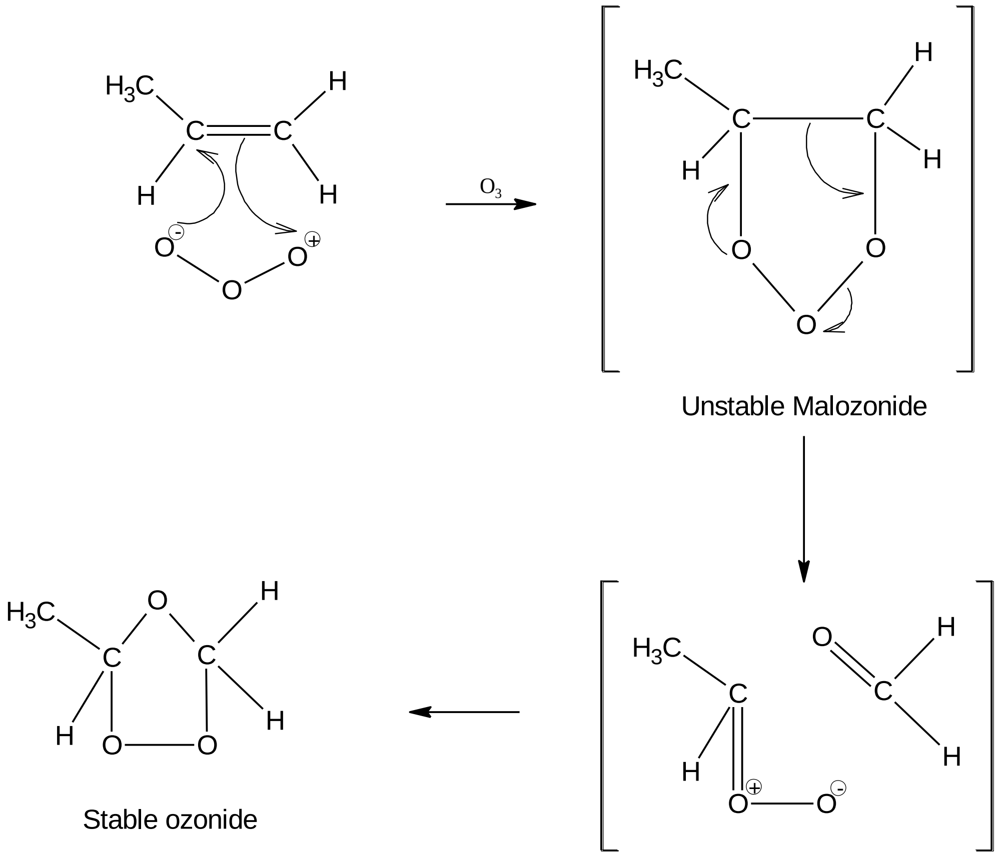

(1)


(2)


(3)

Out of these forms, the dipolar structure (3) undergoes addition with alkane.

In the first step the 1,3 - dipolar form of ozone undergoes a three point cyclic addition with propylene to give the unstable malozonide. Then the malozonide undergoes isomeristaion as shown below to give the stable ozonide.



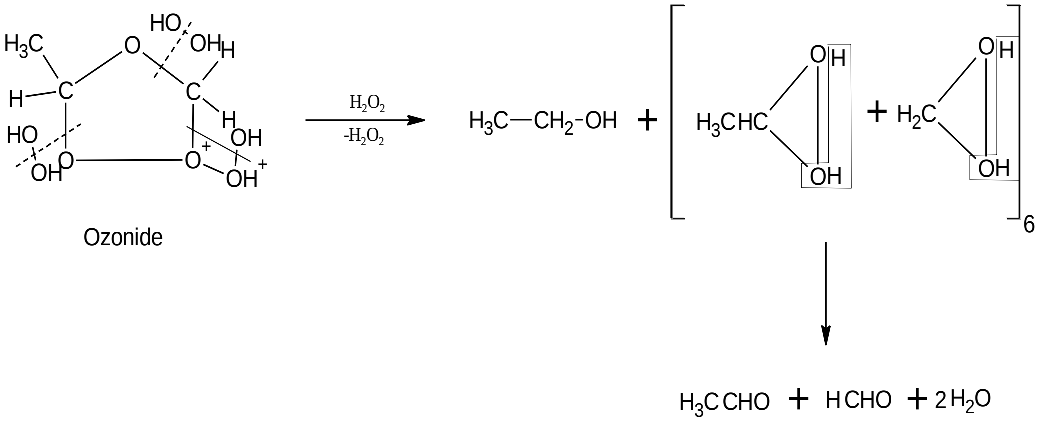
Properties of ozonide.

The ozonides obtained from alkynes are highly explosive. Hence they must be decomposed or converted in to the desired product as soon as they are formed.

Generally ozonides are subjected to the following types of degradations.

1. Hydrolytic cleavage.

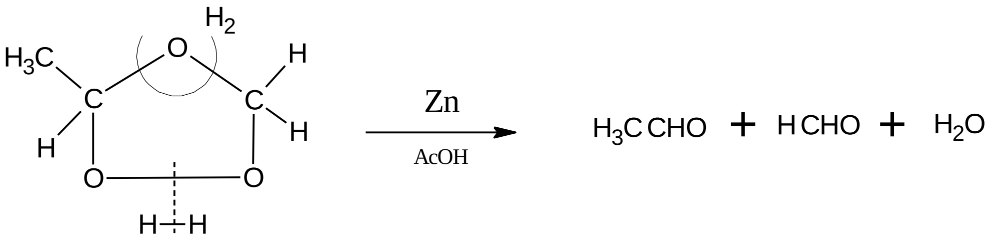
When the ozonides are subjected to hydrolysis, bond cleavage takes place where the double bond was, to give molecules of carbonyl compounds.



In this reaction hydrogen peroxide is obtained as a by product which oxidises the carbonyl compounds to acids. (Therefore the hydrolysis product in this reaction can not be used for the synthesis of carbonyl compounds).

2. Reductive cleavage.

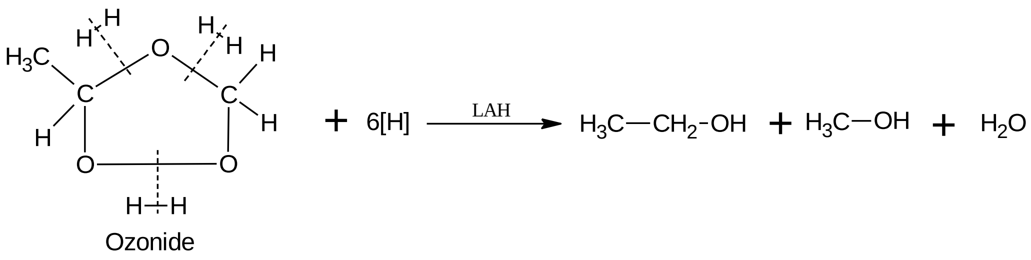
When the ozonide is subjected to reduction in presence of Zn and acetic acid H_2 and Ni or H_2 and Pd cleavage takes place where the double bond was, to give a mixture of carbonyl compounds.



In this degradation reaction, the carbonyl compounds are not converted to acids. Therefore this reaction can be used for the synthesis of aldehyde and ketones.

3. Reduction in presence of LAH.

On the other hand if the ozonides are subjected to degradation in presence of Lithium aluminium hydride (LAH) we get alcohols as shown because the aldehydes and ketones formed first are further reduced by LAH to alcohols as shown below.



Uses of ozonolysis.

It is used in the preparation of aldehydes and ketones.

Used in preparation of alcohols

To determine the position of double bonds in an unsaturated compounds.

To determine the number of double bonds in an unsaturated compounds, on the basis of number of ozone molecules required for ozonolysis reaction.

Determination of the position of double bond in an alkene.

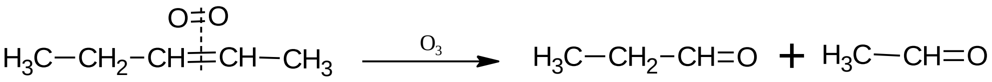
Let us illustrate this by taking pentene with the molecular formula C_5H_{10}, which has only one double bond in it.

It can be a 1- pentene or a 2- pentene which have the following structures.

$$H_3C{-}CH_2{-}CH{=}CH{-}CH_3 \qquad\qquad H_3C{-}CH_2{-}CH_2{-}CH{=}CH_2$$

(1) 2 - pentene (2) 1 - pentene

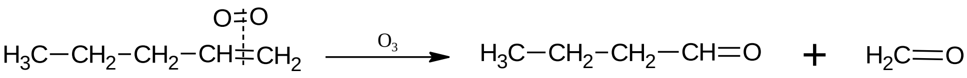
On ozonolysis, if the compound has structure (1) the we get a mixture of propanaldehyde and acetaldehyde as shown below.



$$H_3C{-}CH_2{-}CH{=}CH{-}CH_3 \xrightarrow{O_3} H_3C{-}CH_2{-}CH{=}O + H_3C{-}CH{=}O$$

2 - pentene Propanaldehyde Acetaladehyde

On the other hand if pentene has structure (2), then ozonolysis of it will yield butanaldehyde and formaldehyde as shown below.



$$H_3C{-}CH_2{-}CH_2{-}CH{=}CH_2 \xrightarrow{O_3} H_3C{-}CH_2{-}CH_2{-}CH{=}O + H_2C{=}O$$

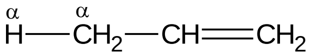
1 - pentene Butanaldehyde Formaldehyde

Thus it is clear that there is only one double bond in pentene because in the ozonolysis reaction only one molecule of ozone is consumed.

More over from the products obtained we can decide the position of the double bond as shown above.

ALLYLIC SUBSTITUTION:

The - carbon attached to a double bonded carbon is called the allylic carbon atom and the hydrogen atom attached to an allylic carbon is called the allylic hydrogen as shown below.



$$\overset{\alpha}{H}-\overset{\alpha}{C}H_2-CH=CH_2$$

Here the C is the allylic carbon and H is the allylic hydrogen.

The substitution reaction taking place on this allylic carbon is called the allylic substitution reactions.

e.g.

$$\underset{\text{Propene}}{H-CH_2-CH=CH_2} \xrightarrow[> 700\ K]{Br_2} \underset{\text{Allyl bromide}}{Br-CH_2-CH=CH_2}$$

At such a high temperature, halogen addition does not take place since at high temperature the addition is a reversible one.

ALLYLIC SUBSTITUTION BY NBS : or

WOHL - ZIEGLER ALLYLIC SUBSTITUTION:

The allylic substitution of propene in presence of N - Bromo Succinimide dissolved in an inert solvent like carbontetra chloride is called the Wohl - Ziegler substitution.

$$H_2C=CH-CH_3 \xrightarrow[h\nu]{NBS/CCl_4} H_2C=CH-CH_2-Br$$

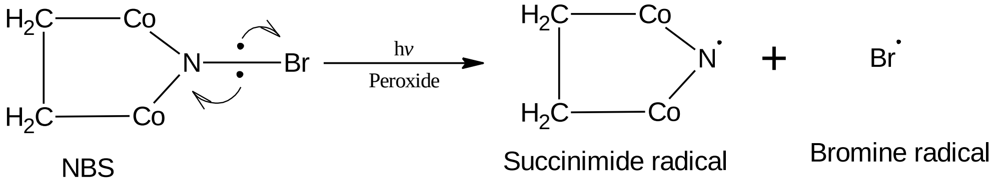
Mechanism of the reaction.

Though the mechanism of this reaction is not certain the following free radical mechanism was suggested.

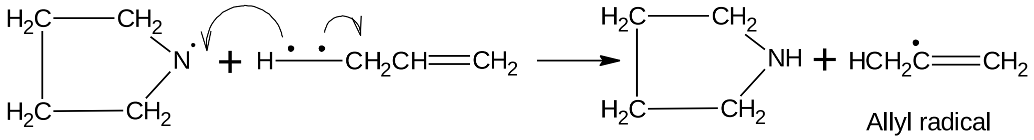
In the first step NBS in presence of sun light or a peroxide gives bromine radical. Then in the second step an allyl free radical is produced which reacts with the bromine free radical to give the product.

The overall reaction can be represented as follows.

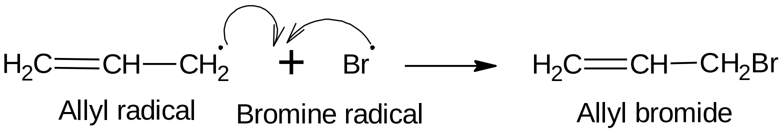
1).



2).

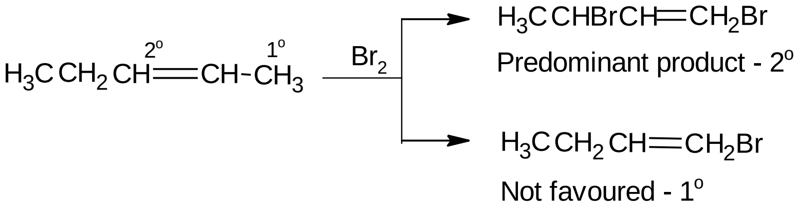


3).



Special feature.

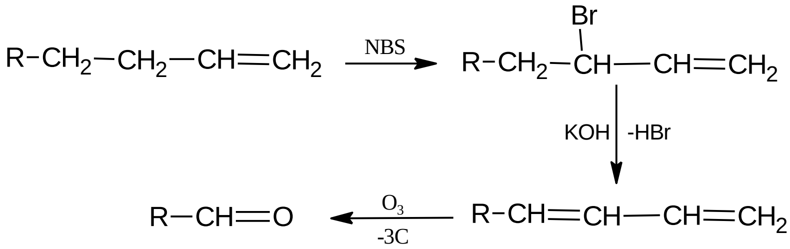
If there are two allyl positions in an alkene then substitution takes predominantly at the more favorable secondary hydrogen than at the less stable primary hydrogen as shown below.



It is obviously because the secondary free radical is more stable than a primary free radical.

USE:

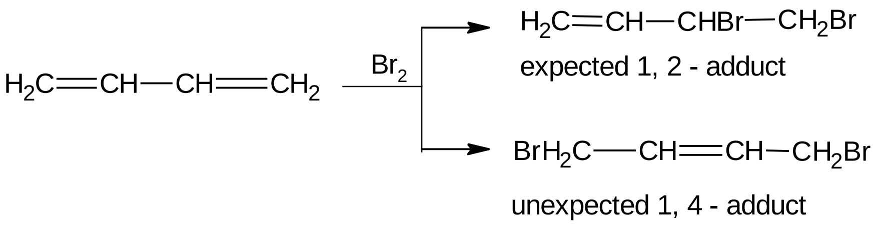
This allylic substitution reaction is very much useful in splitting three carbon atoms from an olefin as shown below.



Here we are getting an aldehyde which has three carbon atoms less than that of the parent alkene which has a synthetic value.

1,2 - and 1, 4 - ADDITIONS:

Though it contains two double bonds, 1,3 - buta diene undergoes addition reaction with halogens like bromine either to give the expected 1,2 - dibromo derivative or the unexpected 1,4 - dibromo derivative and not a tetra bromo derivative as shown below.



Thus invariably a mixture of 1,2 - and 1,4 - adducts are formed. But the relative amount of the product depends on reaction conditions such as nature of addendum, solvent, temperature etc.

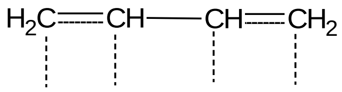
Mechanism of 1,4 - addition.

The formation of 1,4 - addition was explained by the following two ways.

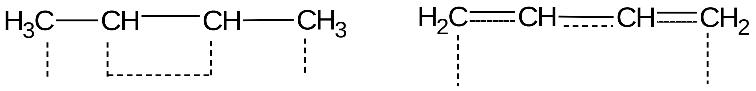
1. Thiel's theory of partial valency.

Thiel suggested a theory called Thiel's theory of partial valency to account for 1,4 - addition.

According to him a single bond is sufficient to hold two carbon atoms together and the two excess pi - bonds are not fully used to link the two carbon atoms. The surplus bond was believed to be shared by all the four carbon atoms. Thiel called this surplus valency as the partial valency or residual valency and represented the nature of partial valency as shown below.



But he opined that the middle partial valencies are engaged and the end partial valencies are free as shown below.



Thus it is obvious that the end carbon atoms are having the partial valencies free and hence more active than the middle ones. As a result the addition of 1,3 - buta diene withe bromine yields the 1,4 - product as shown below.

CH_2-----CH-----CH-----CH_2 + Br_2 CH_2-----H-----CH-----CH_2

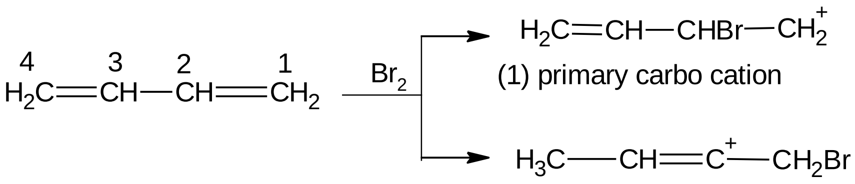
Br Br

CH_2 Br CH CH CH_2Br

1,4 - dibromo butene

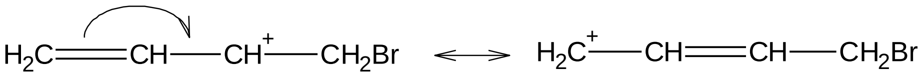
2. Stability of carbo cation.

This reaction follows ionic mechanism as explained below. In the first step the bromine molecule makes an electrophilic attack on the diene to give a carbo cation. In doing so bromine may attack C1 - atom or the C2 - atom to give two different carbo cations as shown below.



(2) secondary carbo cation

But the allyl carbonium ion (2) - being secondary is the most stable one and formed at a higher rate. This carbo cation undergoes the following resonance and thus it is stabilised.



(2) (3)

But out of (2) and (3), (3) is more stable since electronegative bromine atom is placed at a longer distance from the positive charge on the carbon atom. On the other hand in (2) the bromine atom and the positive charge are very close to each other which is not a favoured one.

Though (2) is less stable than (3), if experimental conditions doesn't allow enough time for resonance, (2) reacts with Br$^+$ as soon as it is formed, to give the 1,2 - adduct predominantly (80%) as shown below.

$$H_3C—CH{=}\overset{+}{C}—CH_2Br \xrightarrow{Br^-} H_2C{=}CH—CHBr—CH_2Br$$

(2) (4) - 1, 2 - dibromo butene (80%)

Since 1,2 - bromo butene is formed at a rapid rate it is called the kinetically controlled product.

On the other hand if enough time is allowed for resonance or the reaction is carried out at a higher temperature then 1,4 - product is obtained predominantly (80%) as shown below.

$$CH_2—CH = CH \quad CH_2\,Br \xrightarrow{Br-} CH_2\,BrCH \quad CHCH_2Br$$

(3) (5)

thermo dynamically controlled

1,4 - dibromo butene. (80%)

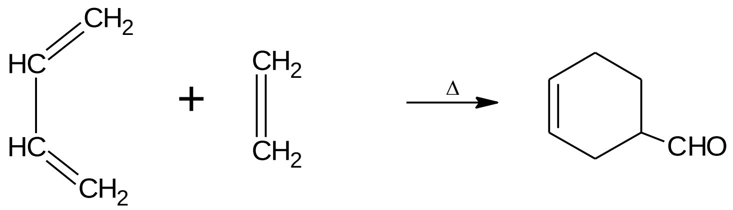
Thus it is clear that at normal conditions kinetically controlled product (4) - is formed to an extent of 80% and at higher temperature the thermodynamically controlled product (5) -is formed to an extent of 80%.

It is because, at higher temperatures the mobility of electrons is very high and so (3) is formed easily and hence the 1,4 - product. Therefore the 1,2 - addition takes place at low temperatures and 1,4 - addition takes place at higher temperatures.

DIEL'S - ALDER REACTION.

The 1,4 - addition of a conjugated diene to an, -unsaturated carbonyl compound just on heating to give a cyclic adduct as shown below is called the Diel's - Alder reaction.

e.g.



(A) - Diene (B) - Dienophile (C) - Adduct

Compound (A) - Diene.

Compound (A) - is a conjugated diene. The diene may be open chain, semi cyclic or a cyclic one.

Compound (B) - Dienophile.

Compound (B) - is called the dienophlile, since it attracts the diene and easily adds to the conjugated diene. A dienophile must be , - unsaturated carbonyl compound or there must be an electro negative group - to the double bond.

Maleic anhydride also acts as a very good dienophile.

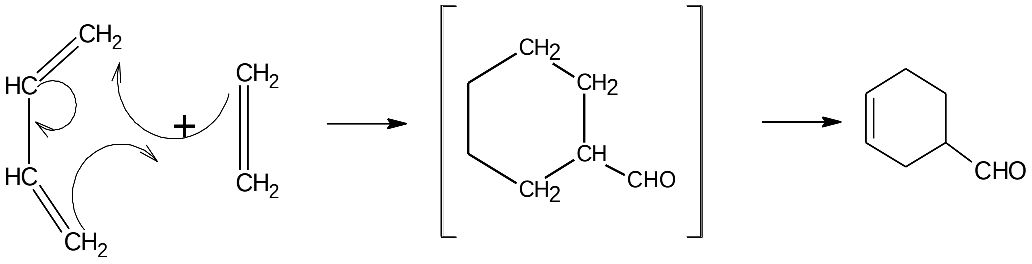
Compound (C) - Adduct.

Compound (C) - is called the adduct and mostly the adducts are six membered ring compounds.

Mechanism of Diel's - Alder reaction.

For this addition no catalyst is needed and just heating the reaction mixtures is enough.

Firstly, the pi - bonds rearrange simultaneously to give a six membered cyclic intermediate. Then this intermediate, changes to the product as shown below.

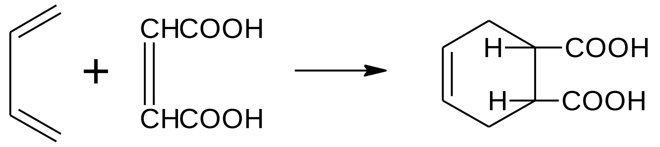


Six membered cyclic intermediate

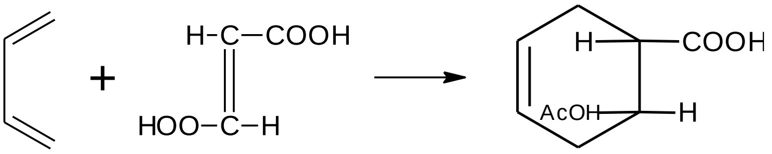
The adduct formed is 1,2,3,6 - tetra hydro benzaldehyde.

Stereo chemistry of Diel's - Alder reaction.

Diel's - Alder reaction takes place only when the double bonds of the diene are in cis - position. But the dienophile may be a cis - or a trans- one.



Cis Cis - form Cis - adduct

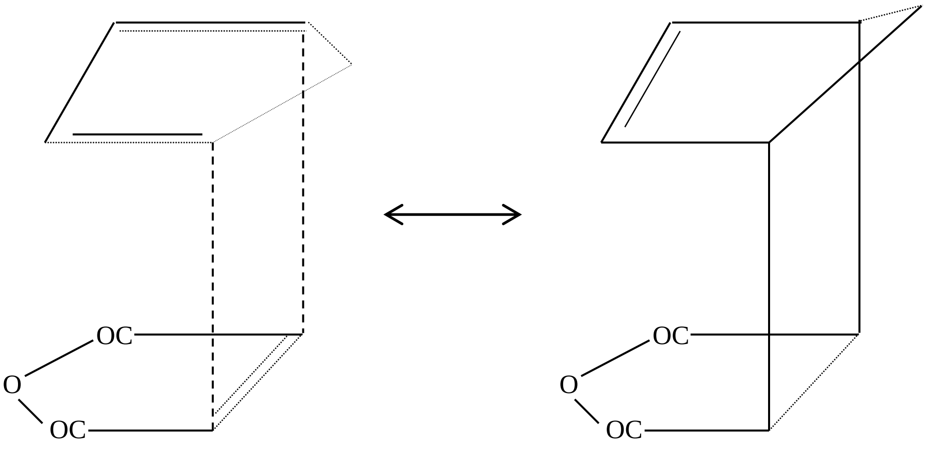


trans - form trans adduct

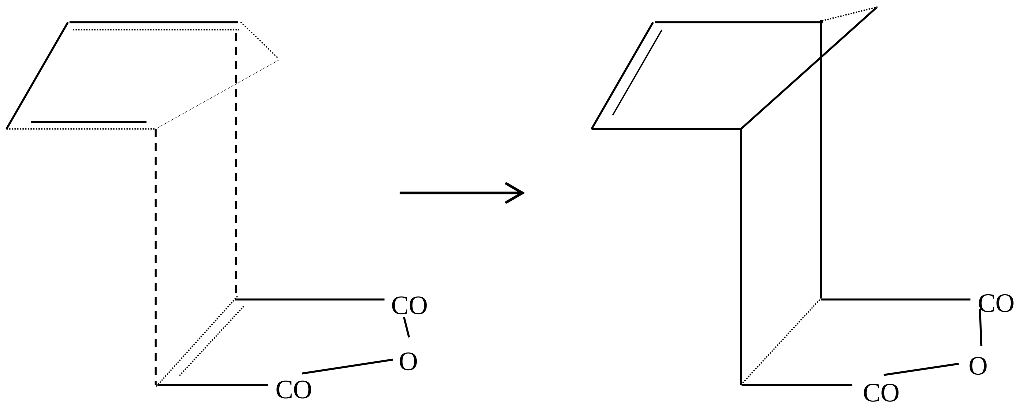
But on the other hand if the reacting diene is in the trans - form the addition doesn't take place.

Kinetically and thermo dynamically controlled products.

If the dienes are cyclic in nature, Two types of addition are possible to give endo - and exo - products as shown below.



(1) endo – cyclic compound



(2) exo – cyclic product

At normal temperatures endo - cyclic product is formed exclusively. Since it is a reversible exothermic addition, increase in temperature, shifts to reactant side. Therefore there is enough time for the exo - product to be formed.

Thus it is clear that the endo - product is the kinetically controlled and the exo - product is the thermodynamically controlled one.

Questions.

1. Which of the o, o - dimethyl p - nitro phenol and m, m - dimethyl p - nitro phenol is more acidic? Why?
2. Which of di - methyl and tri - methyl amine is more basic and why?
3. What is the reason for hydrogen bonding?
4. Glycerin is more viscous. Why?
5. O - nitro phenol is less soluble than p - nitro phenols. Why?
6. Why the molecular weight of benzoic acid is double the theoretical value?
7. Give the resonating structures of tri phenyl methyl carbo cation.
8. When butene is subjected to ozonolysis it gives formaldehyde. Give reason.

NOTES

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

UNIT - IV

INTRODUCTION :

CHEMICAL BODING :

In unit - IV our discussion will be mainly on different types of chemical bonding and their important characteristics.

In ionic bonding we have study about its formation, properties, ion pair effect and the energy of formation of crystals.

In covalent bonding the discussing will be mainly on mode of bond formation, VBT, MOT and the differences between them and the molecular diagrams of certain bivalent molecules like CO, NO and HF.

As for as the co - ordinate bonding is considered, its formation and importance in metal complexes will be discussed.

Then in the second half of the unit classification of hydrides chemistry of some important hydrides and preparation and properties of carbides are given importance.

Finally in noble gases the reason for assigning the name their position in the periodic table and chemistry of Xenon compounds are dealt with.

CHEMICAL BONDING:

Normally there are three types of chemical bonding called ionic bonding, co - valent bonding and co - ordinate bonding which will be discussed in detail as follows.

4.1.1 IONIC BONDS.

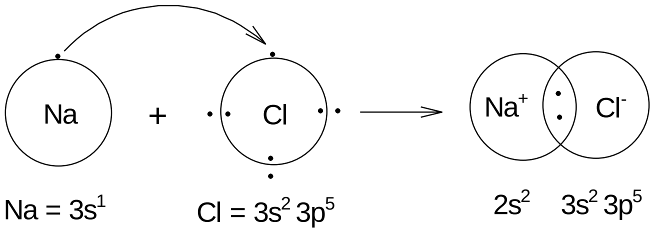
The bond formed by the complete transference of one or more electrons from the outer most energy shell (or valence shell) of one the atom to the valence shell of the other atom is called the ionic bond.

e.g.

For example let us consider the formation of ionic bond between sodium and chlorine to form sodium chloride as follows.

Sodium with atomic number 11, has only one electron in the valence shell and chlorine atom with atomic number 17, has seven electrons in the outer most shell.

Now sodium atom completely transfers the one and only outer most electron to the outermost shell of chlorine atom which can accommodate one more electron, in its valence shell as schematically represented below.



The resultant ions attain the respective nearest inert gas configuration thus become stable. That is sodium attains the electronic configuration of Ne and chlorine attain the electronic configuration of Ar.

The two ions are held intact by the coulomb's law of electrostatic attraction between the sodium ion and the chloride ion.

Since the ionic bonds are formed by electrons which are non directional, the ionic bonds are also non directional and therefore the ionic solids doesn't show any of the isomerisms.

Other example.

F + Ca + F F Ca F

Here two fluorine atoms unit with a calcium atom to give calcium fluoride molecule.

PROPERTIES OF IONIC CRYSTALS:

Since the electrostatic force of attraction is the strongest, the ionic solids are the most stable ones. They have the following characteristic properties.

1. Hardness

Normally completely ionic crystals are very hard in nature. The hardness is attributed to electrostatic force of attraction between the ions. The ions are very close together and intact.

2. Melting point.

Due to the strongest force of attraction in ionic crystals, they are held together very tightly. Therefore an excess of energy is required to break the crystals and bring the ions apart. Then another amount of heat must be spent to melt the solids. As a result, normally the ionic salts have very high melting point as compared to the covalent compounds.

More over the melting point of ionic solids is very sharp. They also have low volatility.

3. Conductance of electricity:

Though the ionic solids are built up only of ions, they do not conduct electricity in the solid state. It is because, the cation and the anion are very tightly held due to electrostatic force attraction and so they are unable to move considerable distance when an electric field is applied.

But in the molten state, the kinetic energy of the ions is raised and as a result the mobility of the ions are more than enough to move freely and so conduct electricity.

4. Solubility.

Ionic salts are highly soluble in water but difficultly soluble in organic solvents. This is because,

a). Water having high dielectric constant, attracts strongly the ions of crystals and hence they easily separate individually from one another and go into solution.

b). In going in to solution the freedom of movement for ions is largely increased and hence become more stable in solutions.

c). Water acts a very good dipole. Therefore the +ve end of the dipole attracts the -ve ion and the-ve end of the dipole attracts the +ve end of ion. This also facilitates the solubility of ionic crystals.

On the other hand, organic solvents have very low dielectric constants and so act as a weak dipoles.

INERT PAIR EFFECT:

The reluctance to form bonds, by the pair of valence shell electrons of certain elements is called the inert pair effect.

That is Group - I elements give invariably mono valency and Group - II elements give divalency.

But for example Group - III and Group - IV elements are reluctant to give their group valencies III and IV respectively. Sidgwick put forward an argument that such elements with inert pair, form the more stable oxidation state which is two less than their group valencies.

That is Group - III elements give the oxidation state of (3-2) which is equal to 1 and the group - IV elements give the oxidation states of (4-2) which is equal to 2, along with their usual group valencies.

More over the lower valencies are more stable than their higher valencies. This fact is explained by the inert pair effect as detailed below.

The electronic configuration of Tin and Lead of group - IV elements can be represented as follows.

Sn = 2,8,18,18,4 and

Pb = 2,8,18,32,18,4.

Thus the outer shell configuration of these two elements are found to be

ns^2np^2.

Therefore Sn^{2+} and Pb^{2+} must have the electronic configuration of

ns^2np^o

Thus +2 state of these elements have a configuration of ns^2, in which the electron have a paired structure which is more stable. As a result it becomes very difficult to break the pair for bond formation. Therefore the +II state is more stable than the +IV state.

Similarly Galium, Indium and Thalium of group III elements have a normal group valency of 3. But the +1 oxidation state of the elements more stable than the previous one. This is also due to the inert pair effect as explained below.

The general electronic configuration of these elements is

ns^2np^1.

In their +I valency state, the electronic configuration will be

ns^2np^0.

Now it becomes very difficult to un pair the stable ns^2 electronic structure to form the usual oxidation state of +III, because of the inert pair effect.

If the energy required to un pair the s - electron exceeds the energy evolved in the bond formation, then the electrons remain paired. On the other hand if the energy of bond formation exceeds the energy required to un pair the electrons, then un pairing takes place and the +III is attained.

LATTICE ENERGY OF IONIC SOLIDS:

The amount of energy released, when a cation and an anion in their gaseous states are brought from infinity to their respective lattice sites in a crystal to form one mole of an ionic solid is called the lattice energy of that solid.

e.g

$$A^{+}_{(g)} + B^{-}_{(g)} \longrightarrow A^{+}B^{-}_{(S)} + U$$; (U = lattice energy)

where $A^{+}_{(g)}$ is the cation in the gaseous state, $B^{-}_{(g)}$ is anion in the gaseous state and U is the lattice energy of the crystal.

BORN - HABER CYCLE: or

The experimental determination of lattice energy.

The chemical process indirectly used with the help of thermodynamics to calculate the lattice energy of an ionic crystal is called the Born - Haber cycle.

We can explain various steps involved in the calculation of lattice energy using Born - Haber cycle, by taking for example the formation of NaCl crystals as shown below.

Energy associated with

1. The conversion of metallic sodium in to gaseous sodium atom.

(Sublimation energy)

The energy required to convert one mole of metallic sodium into gaseous sodium atom called the sublimation energy 's' is given by the following equation.

$$Na_{(S)} + S \longrightarrow Na_{(g)}$$

Where 's' is the sublimation energy.

2. The conversion of gaseous chlorine molecule in to gaseous atom.

(Dissociation energy)

The energy required to dissociate one molecule of chlorine into gaseous chlorine atom called the dissociation energy is given by the following equation.

$$Cl_{(2)} + D \longrightarrow 2Cl_{(g)}$$

where 'D' is the dissociation energy.

In this reaction, two gaseous atoms of chlorine are produced. But we need only one gaseous atom of chlorine. Therefore the dissociation of required to produce one gaseous atom of chlorine = D/2.

3. The conversion gaseous sodium atom into gaseous ion.

(Ionisation energy)

The energy required to convert one atom of gaseous sodium in to one gaseous ion, called the ionisation energy is given by,

$$Na_{(g)} \ + \ IE \longrightarrow Na_{(g)} \ + \ e^{-}$$

where IE is the ionisation energy of ionisation potential.

4. The conversion of gaseous chlorine atom in to gaseous chlorine ion.

(Electron affinity)

The energy required for this change is called the affinity energy of electron affinity and given by the chemical equation,

$$Cl_{(g)} \ + \ e^{-} \longrightarrow Cl\text{-}_{(g)} \ + \ EA$$

Where EA is the electron affinity or affinity energy.

5. Combination of gaseous ions to give the solid crystal.

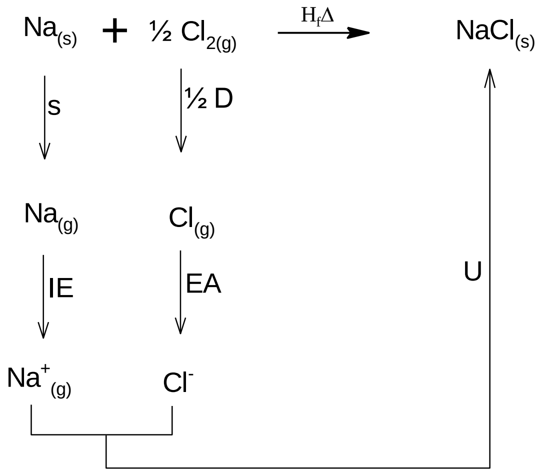
(Lattice energy)

Finally the +ve and the -ve gaseous ions are brought together to give the solid crystal. In this process energy is released which is called the lattice energy as given below.

$$Na_{(g)} \ + \ Cl_{(g)} \longrightarrow NaCl_{(S)} \ + \ U$$

Where U is the lattice energy released.

The overall enthalpy of formation of NaCl, in the form of Born - Haber cycle can be represented as follows.



Born Haber cycle for the formation of $NaCl_{(s)}$

According to Hess's law, the enthalpy of formation of any compound must be same, irrespective of the path by which it is formed.

$$H_f = S + 1/2\,D + IE + EA + U$$

In this equation all the values except 'U' is known and hence it can be calculated from all other values which can be obtained experimentally.

e.g.

The lattice energy of NaCl can be calculated from all other observed values as follows.

Practically it was found that,

$S = 108.5$ kJ mol^{-1}

$D = 243.0$ kJ mol^{-1}

$IE = 495.2$ kJ mol^{-1}

$EA = -348.3$ kJ mol^{-1}

$H_f = -381.8$ kJ mol^{-1}

By substituting these values in the equation,

$$H_f = S + 1/2\,D + IE + EA + U$$

We get,

$$-381.8 = 108.5 + 1/2(243.0) + 495.2 - 348.3 + U$$

i.e. $-381.8 = 376.9 + U$

or $U = 376.9 + 381.8$

$U = 758.7 \text{ kJ mol}^{-1}$

Thus the lattice energy of NaCl crystal is = $758.7 \text{ kJ mol}^{-1}$

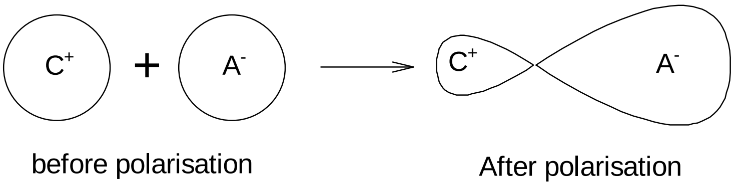
POLARISATON OF IONS:

For a very long period, it was believed that, covalent and ionic bonds are entirely different from each other. But now a days, it is seen that, it is not so always. That is in many cases, an ionic bond has some co - valent character and a covalent bond has some ionic character.

This type of intermediate bond formation was explained by a phenomenon called polarisation.

"The distortion or deformation of the electronic cloud, when a cation and an anion approach each other is called polarisation".

For example, let us take an ionic compound C+ A- and say that C+ is small in size than A-. Since C^+ is small in size, it has greater affinity for electrons than A- ion and as a result, the electron cloud of the anion is distorted and attracted towards the cation as shown below.



As a result, the electron cloud in A- is not spherical but distorted or polarised.

Here C+ ion is said to polarise and A- is said to be polarised by the cation.

This polarisation of ions result in high concentration of electron density between the nuclei, which result in the formation of a covalent bond.

This type of covalent bond is called polar covalent bond and it was found that, a polar covalent bond is more stable than a pure covalent or pure ionic bond.

FAJAN’S RULE:

(or Factors affecting polarisation)

The extent of polarisation must evidently depend on the polarising power of the cation and the polarisability of the anion.

To explain the extent of polarisation, Fajan phramed a rule called Fajan’s rule which can be detailed as follows.

1. Size of the cation.

The smaller the size of cation, the higher is its polarising power. It is because, a smaller cation has its +ve charge concentration in smaller area resulting in high charge density. Therefore these ions distort the electronic cloud of the anion very effectively.

2. Size of the anion.

The larger the size of anion, the greater is its polarisability. It is because, the distance between the proton and the outer shell electron being greater, the electrostatic force of attraction is weaker. So the electrons are easily distorted or polarised.

3. Charge on the ions.

As the charge on the cation increases, its polarising power obviously increases due to its higher +ve charge and smaller size.

If the charge on the anion is high, then its polarisability increases, because of its larger size and higher electron density.

4. Nature of the cation.

Cations with $ns^2np^6nd^{10}$ configuration, that is 18 - electron configuration have higher poarisation than the cations with 8 - electron configurations.

For example, Cu^{2+} ion with 18 - electron configuration polarises more than a Na^+ ion with 8 - electron configuration.

The reason is that, the effective nuclear charge on the former atom is high and in the later is low.

5. Nature of solvent.

When the dielectric constant of the solvent is greater, then the solvent doesn’t allow the ions in solution to attain covalent character. In other words, polarisability of the anion decreases.

IMPORTANCE OF POLARISATION:

(or Applications of polarisation)

1. Hardness.

We know that, the hardness of crystals is attributed to its ionic character. Therefore, increase in polarisation increases the covalent character and hence decreases the hardness of the crystals.

2. Stability

Bromides and Iodides which are covalent in nature, have higher lattice energy and consequently higher stability than that expected from theoretical values.

It is because, the anions are easily polarised to polar covalent bonds, which are more stable than the pure ionic bonds.

3. Solubility.

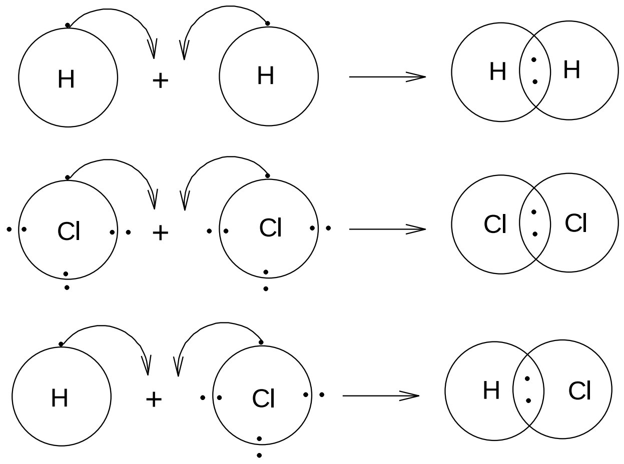
The solubility of ionic solids in a polar solvent decreases with increase in the degree of polarisation of the ionic solid. This is because increase in polarisation, increases the covalent character which results in decreases in solubility in polar solvents. But their solubility will be higher in non polar solvents.

For example AgCl which is ionic is water soluble where as the bromide and the iodide which are covalent in nature are water insoluble.

4.1.2 - COVALENT BOND:

The bond formed between atoms by mutual sharing of electrons, each atom contributing one, is called the covalent bond.

e.g.



In this process, the combining atoms acquire their respective nearest noble gas configurations so that they gain stability. Hydrogen atom attains the electronic configuration of He and chlorine atom that of Ar.

COVALENCY:

According to Lewis concept, the number of electrons that an atom contribute to form covalent bond is called its covalency.

Thus the covalency of H = 1,

O = 2 and

C = 4.

CHARACTERISTICS OF COVALENT BONDS:

(or Properties of covalent bonds)

1. State of existence.

Since there is no transfer of electrons during covalent bond formation, covalent compounds exist as molecules and not as ions.

2. Conductance of electricity.

Since covalent compounds are not ionic, they don't conduct electricity.

3. Melting and boiling points.

Most of the covalent compounds are gases, or liquids with low boiling points. Some of them are solids, but with low melting point. The low boiling and melting points are due to the fact that, the inter molecular force of attraction is very weak and hence they are easily broken even at low temperatures.

4. Solubility.

Covalent compounds are less soluble or even insoluble in polar solvents like water. But they are freely soluble in non polar solvents like benzene carbon tetra chloride etc.

5. Directional characteristics.

Covalent bonds are rigid and directional in nature. Therefore they show position and stereo isomerism.

VALENCE BOND THEORY:

The formation of covalent bonds simply by mutual sharing of electrons doesn't answer the following questions namely,

1. Why a covalent bond is formed?,
2. How are shared electrons ar arranged in a molecule?,
3. What are the forces of attraction that make a covalent molecule stable? and
4. How are the compounds such as PF_6 and BF_3 in which the central atoms have more or less than 8 - valence electrons, stable?

The answer to these questions is given on the basis of modern theories like Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT).

The valence bond theory was put forward by W . Heitler in 1927 to explain the stability of covalently formed hydrogen molecule and later it was developed by Linus Pauling for which who was awarded Nobel prize in 1954.

This theory provides, a basis for the simple description of bonds in small in - organic molecules. According to VBT,

1. Atoms are considered to retain their individuality in the molecules.
2. Completely filled orbitals of the atoms remain intact. That is they doesn't take part in the bond formation.
3. Only unpaired electrons of one atom tend to combine with the unpaired electron with same symmetry of another atom.
4. As a result of this, the atom attain a stable configuration of the nearest inert gas.
5. The number covalent bonds formed by an atom is normally equal to the number of unpaired electrons on it in the ground state. How ever in certain cases, atoms form more bonds than the number of unpaired electrons due to the excitation of electrons to the higher state.
6. The spin of two electrons involved in bond formation must be opposite in spin.
7. Electrons that are paired in the valence shell are called lone pair of electrons.
8. The shape of the molecule is determined by the direction by which the overlapping orbitals are pointing.

PAULING - SLATER'S THEORY:

Later on the theory was extended further by J.C.Slater and L.Pauling who utilised the following wave mechanical principles.

1. If $\square_A$ and $\square_B$ are the wave function for any two completely independent system A and B, then their total wave function will be given as,

$$\square = \square_A + \square_B$$

2. Similarly the total energy of the independent system A and B will be equal to the sum of the individual system as,

$$E = E_A + E_B$$

Where E = total energy of the system,

E_A = energy of the system A and

E_B = energy of the system B.

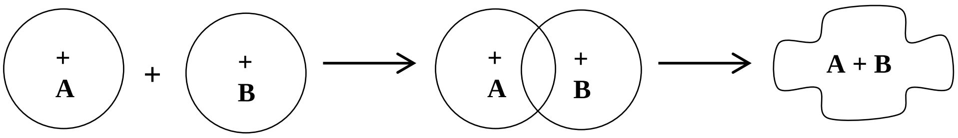
DIFFERENT TYPES OF OVERLAP:

(or Formation of sigma - and pi - bonds)

π - bond.

The bond formed by the axial overlap of two atomic orbitals to give a molecular orbital is called the sigma bond.

e.g.

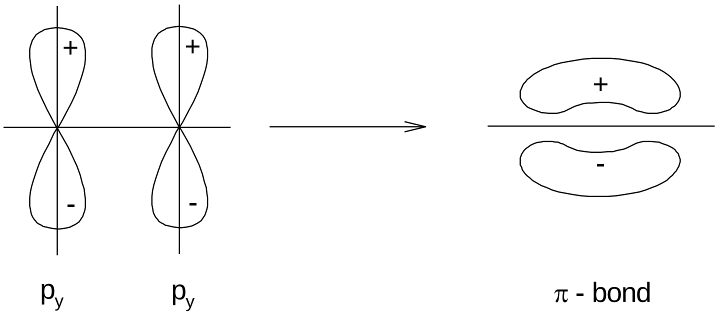


s – atomic orbitals after overlapping σ-bond

A sigma bond is formed between a s - and s- orbital a s - and any p - orbital or a p_x and a p_x orbital only by axial overlaps.

π - bond.

A bond formed by the lateral overlap of two atomic orbitals is called a - bond. A bond is formed between a p_y and a p_y or between a p_z and a p_z bond as shown below.



From the above representations it is clear that, the atomic orbitals completely loose their identity.

LINEAR COMBINATION OF ATOMIC ORBITALS, (LCAO):

The combination of atomic orbitals to give a molecular orbital called the linear combination atomic orbitals.

There are two types of linear combinations of atomic orbitals called 1. Additive combination and

2. Subtractive combination.

To explain this, let us consider two atomic orbitals whose wave functions are - and .

During their linear combinations these atomic orbitals may yield two molecular orbitals namely and where,

= +

= -

Here is the molecular orbital formed by the additive combination of atomic orbitals, whose energy E^+ is lower than that of either or

This molecular orbital with lower energy than the atomic orbitals is called the Bonding Molecular Orbital (BMO).

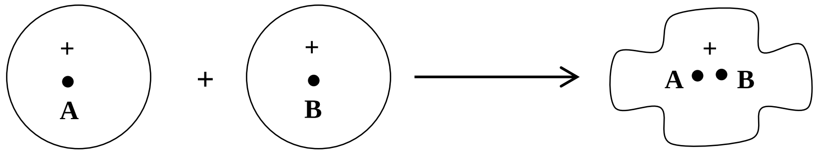
is the molecular orbital formed by the subtractive combination of atomic orbitals, whose energy E- is higher than that or either or

This molecular orbital with higher energy than the atomic orbitals is called the Anti Bonding Molecular Orbital (ABMO).

Electron density in bonding and anti bonding orbitals.

The electron density of bonding molecular orbitals can be represent as follows.

σ - BMO in s - orbitals.

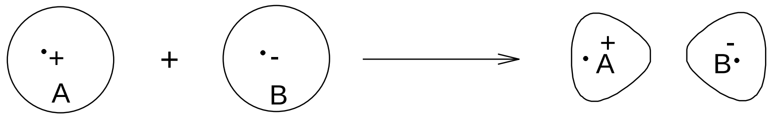


s – atomic orbitals

Electron density in σ-bonding orbitals

It is clear from the above representations that in the - bonding molecular orbital the electron density is in between the nuclei.

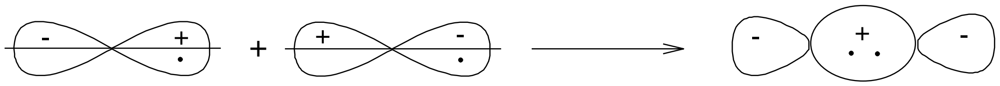
σ - anti bonding molecular orbital.



s - atomic orbitals

σ* anti bonding molecular orbital

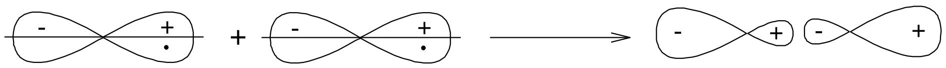
σ - BMO in p_X - orbitals.



p_x - atomic orbitals

σ - bonding orbital

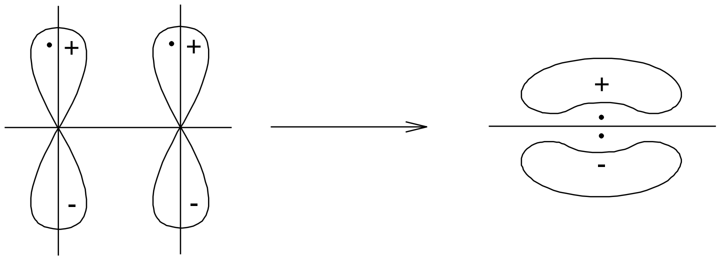
$\sigma*$ - ABMO in p_X - orbitals.



p_x - atomic orbitals

σ* - anti bonding molecular orbital

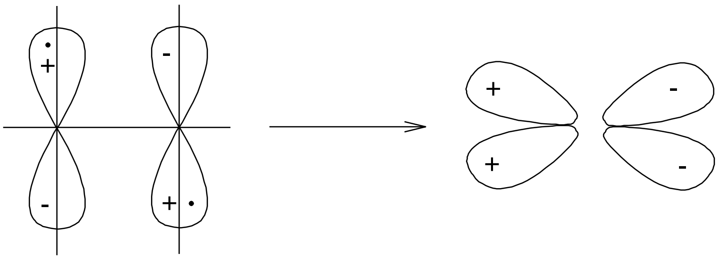
π - bonding orbital.



p_y - atomic orbitals

electron density in π - bonding orbital

π* - ABMO in p_y - atomic orbitals.



p_y - atomic orbitals

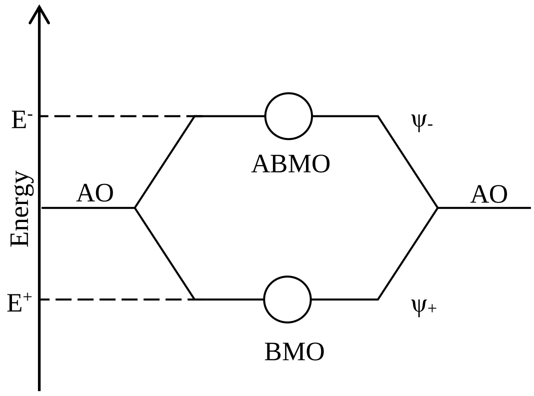
π* - anti bonding orbital

The bonding molecular orbitals are represented without any superscript namely - and -,where as the anti bonding molecular orbitals are represented with a superscript on the respective orbitals as

- and.

The extent of lowering of energy of BMOs, when compared to the energy of atomic orbitals is, more or less equal to the increase in energy of the ABMOs.

The energy level diagrams of BMOs and the ABMOs can be represented as follows.



CONDITIONS FOR THE COMBINATION OF AOs.

It should be noted that two AOs essentially will not combine with each other to give a MO. There are some limitations for atomic orbitals to combine, as listed below.

1. The energy of the combining AOs must be more or less equal. That is, 1s - orbital of an atom can’t combine with the 2s - orbital of another atom of the same element. But in the case of hetero nuclear diatomic molecules, this type of combination is possible.
2. In a similar way the combining atomic orbitals must have the symmetry. That is a p_y - orbital can’t combine with a p_z - orbital.
3. The AOs combine to give a MO, only if the overlap is considerable.

Difference between AOs and MOs.

Atomic orbitals	Molecular orbitals
Electron in an atomic orbital is influenced by only one nucleus.	Electron in a MO is influenced by one more nuclei.
Energy of the electron in an atomic orbital will comparatively high.	Energy of the electrons in a MO is lower than that of the corresponding AOs.
Atomic orbitals retain their identity.	AOs loose their identity completely after forming MOs.

Difference between BMO and ABMO.

BMO	ABMO
BMO is formed by the additive overlap of AOs.	ABMO is formed by the subtractive overlap of AOs.
It has lower energy than the AOs from which it is formed.	It has higher energy than the AOs from which it is formed.
Therefore the BMOs are more stable than the AOs.	But the ABMOs are less stable than the respective AOs from which it is formed.
The electron density between the nuclei is high. So the	The electron density is very low in between the nuclei and so the

repulsive force between nuclei is low. Hence the BMOs favour stable bond formation	repulsive force will be high. ABMOs are against bond formation.

POSTULATES OF MOT:

The second approach to the problem of covalent bonds by wave mechanical treatment was by the Molecular Orbital Theory (MOT). The basic principles of MOT, are as follows.

1. When nuclei of two atoms come close together, their atomic orbitals interact to give MOs.
2. Number of MOs formed is equal to the total number of AOs that take part in formation of MOs.
3. The AOs loose their identity completely, after the formation of the MOs.
4. Each molecular orbital is described by a wave function □□□ - known as molecular orbital wave function.
5. The MO wave function □□□ - is such that □□□ ^{2} -represents the electron density.
6. Each MO wave - is associated with a set of quantum numbers which determine the energy and shape of the MOs.
7. Each wave is associated with definite energy and the total energy of the molecule is the sum of the energy of filled MOs.
8. Electron density lie in between the nuclei.
9. Each electron in a molecular orbital belongs to all the nuclei present in the molecule.
10. Electrons fill the MOs in the same way as that followed in filling the AOs. That is the *aufbau* principle and Pauling’s exclusion principle are followed in filling MOs.
11. Like AOs the MOs can also have a maximum of two electrons per orbital.
12. Electrons moving in an orbital must have opposite spin value of +1/2 or -1/2.

TABULATION OF VARIOUSMOs FORMED FROM AOs.

We know that we get two MOs from two AOs designated as bonding and anti bonding MOs. If the AOs participating are 1s - orbitals then the MOs obtained are,

□ (1s) and □□(1s)

Similarly the second shell orbitals namely 2s - and 2p - AOs can give 8 MOs as shown below.

2s $\longrightarrow$ σ(2s) and σ*(2s)

$2p_x$ $\longrightarrow$ $\sigma(2p_x)$ and $\sigma^*(2p_x)$

$2p_y$ $\longrightarrow$ $\pi(2p_y)$ and $\pi^*(2p_y)$

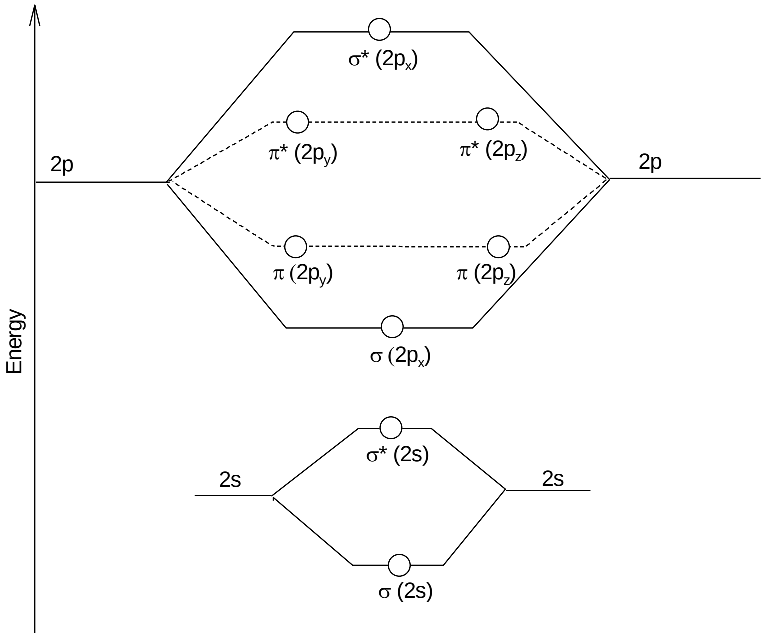
$2p_z$ $\longrightarrow$ $\pi(2p_z)$ and $\pi^*(2p_z)$

Energy level diagram or MOs.

The energy levels of the MOs are determined experimentally from spectroscopic data. It was found that the energies of various MOs are in the following increasing order.

$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_x) < \pi(2p_y) = \pi(2p_z) < \pi^*(2p_y) = \pi^*(2p_z) < \sigma^*(2p_x)$.

This fact can be diagrammatically represented as follows.



Energy level diagram of various BMOs and ABMOs.

But this energy sequence is not always true.

BOND ORDER:

Bond order of a molecule is defined as, half the quantity of the difference between the number of electrons in BMO and the number of electrons in ABMO.

Mathematically,

Bond order = 1/2 (number of electrons in BMO - number of electrons in ABMO)

For example, there are two electrons in BMO and no electrons in the ABMO of Hydrogen molecule. Therefore the

Bond order in H_2 = 1/2 (2 - 0) i.e. 1/2 (2)

= 1.

Thus hydrogen molecule has one bond.

Similarly in Helium molecule there are two electrons in BMO and two electrons in the ABMO. Therefore the,

Bind order in He = 1/2 (2 - 2) i.e. = 1/2 (0)

= 0 .

Thus the Helium molecule has no bond and hence it is mono atomic in nature.

Generally the bond orders 1, 2, and 3 corresponds to single, double and triple bonds.

Effect of bond order.

Bond order of molecule reveals the amount of bond energy of that molecule. That is higher the bond order, the higher the bond energy of the molecule. In other words the bond dissociation energy of a molecule is directly proportional to its bond order.

But the bond length is inversely proportional to the bond order of the molecule. That is higher the bond order, the shorter the bond length.

Rules for adding electrons to MOs.

Molecules are built up of adding electrons to molecular orbitals, just as electrons are added to AOs. Therefore in building up of MOs, the same aufbau principle used in filling up of AOs is also followed here as said below.

1. The MO with lowest energy is filled first.
2. The maximum number of electrons in a MO is two only.
3. The spin of two electrons in a MO must have opposite spins only. That is they must be placed paired.
4. If there are two or more degenerate orbitals, that is orbitals with same energy, pairing of electrons in MO will take place, only after each orbital of same energy has one electron each.

Electronic configuration of MOs.

The electronic configuration of a MO is given by taking in to account of the total number of valence electrons of the combining AOs.

For example, let us consider the MO of H_2 molecule. The atomic number z of H - is 1 and therefore the electronic configuration is,

$H = 1s^1$

Thus a total of 2 electrons are to be accommodated in the MO of H_2.

Therefore the electronic configuration of MO of H_2 is given as,

$H_2 = \square\ (1s^2)$

e.g. 2.

The atomic number ‘z’ of Lithium atom is 3 and therefore the electronic configuration is

$Li = 1s^2\ 2s^1$

Therefore a total of six electrons are present in the Lithium molecule. But out of this six electrons, four are present in the inner K shell. These inner shell electrons are not disturbed during bond formation and therefore need not be considered in arriving the electronic configuration of MO. But these are denoted by ‘KK’, in the configuration, meaning that they are fully filled inner shells.

Thus the electronic configuration of MO of LI is,

$Li_2 = KK\ \square\ (1s^2)$

e.g. 3.

The electronic configuration of N_2 molecule whose atomic number is 7 may be written as shown below.

For N ‘z’ = 7 : $1s_2\ 2s_2\ 2p^3$

Therefore we have to account for ten valence shell electrons and so electron structure is

N_2 = KK □ $(2s^2)$ □$^{\square}$ $(2s_2)$ □ $(2p_x^2)$ □ $(2p_y^2)$ □ $(2p_z^2)$

MO diagrams of some diatomic molecules.

Molecules formed by the combination of two atoms are called the ‘diatomic’ molecule.

e.g.

H_2 , N_2 CO, NO

If the two atoms forming the molecule are of same kind then that molecule is called the ‘homo diatomic’ molecule.

e.g.

H_2, Cl_2

If the two atoms forming the molecule are of different kind, then that molecule is called the hetero diatomic molecule.

e.g.

CO, HF

MO - applied to hetero diatomic molecules.

MO - of CO.

The atomic number ‘z’ of carbon atom is six and therefore its electronic configuration is ,

C $=1s^2\ 2s^2\ 2p^2$

and the atomic number of O is eight and hence its electronic conflagration must be,

O = $1s^2\ 2s^2\ 2p^4$

Thus there four electrons in the valence of Carbon and six electrons in the valence shell of Oxygen which totals ten electrons.

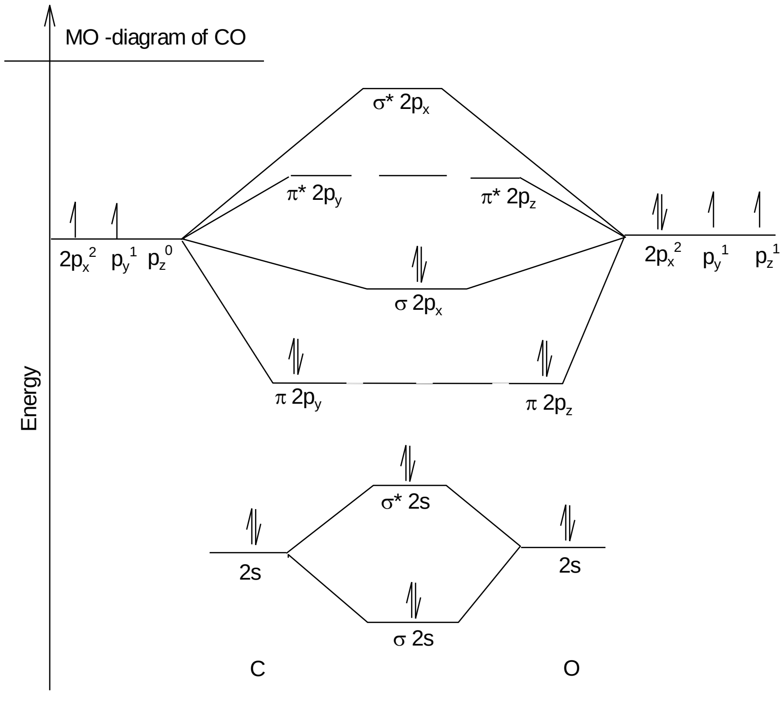
Therefore we have to accommodate this ten electrons in the MO of CO.

Due to higher electronegativity, the energy of AO of Oxygen will be lower than that of carbon. But if there is energy difference between the atomic orbitals, then the BMO will receive more energy contribution of the low energy AO and the ABMO will have more energy contribution of high energy AO.

Therefore the BMO will receive more energy contribution from low energy Oxygen AO and the ABMO will receive more energy contribution from high energy carbon AO.

In other words the BMO will be closer to Oxygen in energy and the ABMO will be closer in energy to that of Carbon AO, which can be shown by the following diagram.

MO - diagram of CO



The BMO will have more characteristics of oxygen AO and the ABMO will have more characteristics of Carbon AO.

The electronic configuration of CO molecule can written as follows.

$\text{CO} = \text{KK}\ \square\ (2s^2)\ \square^{\square}\ (2s^2)\ \square\ (2p_x^2)\ \square\ (2p_y^2)\ \square\ (2p_x^2)$

Here $(2p_x^2)$ is having higher energy than the $(2P_x^2) = (2p_z^2)$ MOs, because of the mixing of orbitals.

Bond order.

Number of electrons in BMO = 8

Number of electrons in ABMO = 2

Bond order = 1/2(8 - 2)

= 3.

Thus Nitrogen molecule contains three bonds out of which two are sigma - bonds and one is pi - bond.

Magnetic property.

From the electronic configuration of MO of CO it is clear that, there is no unpaired electron in any of the MOs and therefore CO molecule is diamagnetic in nature.

MO diagram of NO.

The atomic number ‘z’ of Nitrogen atom is 7, and therefore its electronic configuration must be as follows.

$N = 1s^2\ 2s^2\ 2p^3$

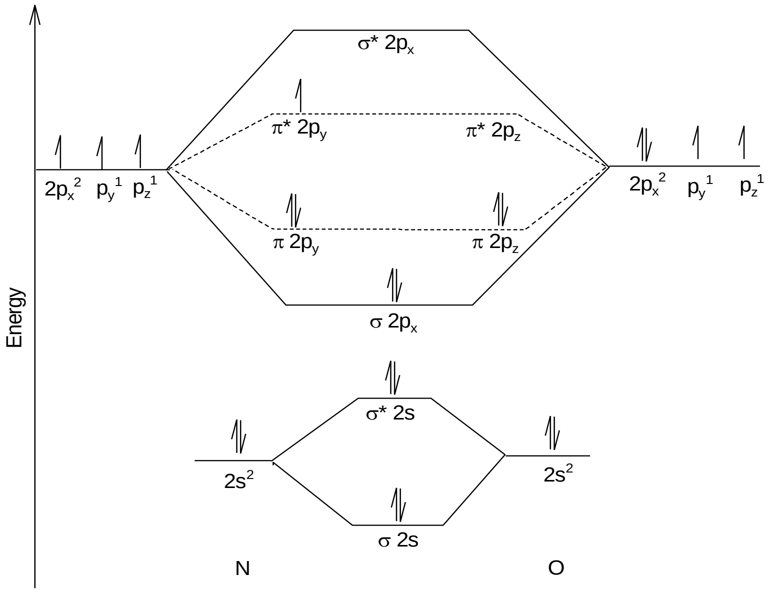
The atomic number ‘z’ of Oxygen is 8, and therefore its electronic configuration must be as,

$O = 1s^2\ 2s^2\ 2p^4$

There are a total of 11 electrons and hence we have to accommodate for all of them in arriving the MO.

As a result the MO diagram of NO molecule will take the following form.

MO -diagram of NO



Here the BMO will contribute more to the AO of Oxygen and the ABMO will contribute more to the AO of Nitrogen.

The electronic configuration of the MO of NO can be written as follows.

NO = KK □ $(2s_2)$ □□ $(2s_2)$ □ $(2p_x^2)$ □ $(2p_y^2)$ □ $(2p_z^2)$ □□ $(2p_y^1)$

Bond order.

The bond order in NO molecule is

= 1/2 (number electrons in BMO - number of electrons in ABMO)

= 1/2 (8 - 3)

i.e. = 2.5

Thus the number of bonds in NO is 2.5 where as it is 3 in N_2

Magnetic property of NO.

Since in NO molecule there is an unpaired electron in the ABMO, this molecule has paramagnetic property.

MO diagram of HF:

The atomic number ‘z’ of H - atom is one and therefore its electronic configuration will be as follows.

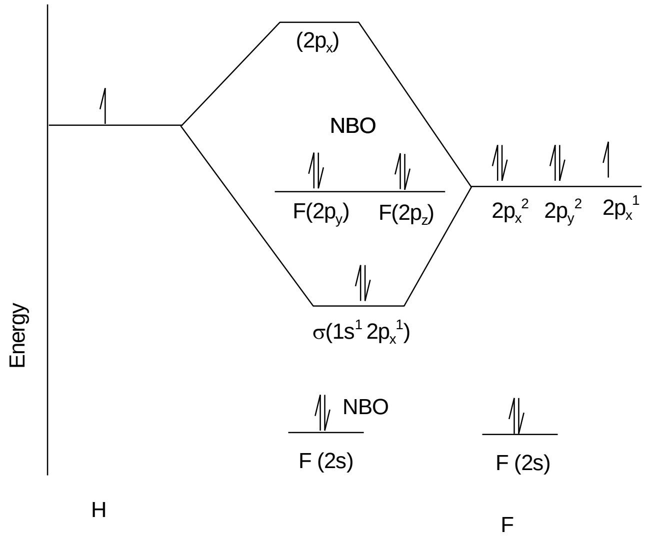
H = $1s^1$

The atomic number ‘z’ of fluorine is 9 and therefore its electronic configuration must be as follows.

F = $1s^2\ 2s^2\ 2p^5$

In HF molecule only the 2p - electrons of F- effectively combine with the solitary electron of Hydrogen atom. That is the $1s^1$ electron of H - atom combine with the $2p_Z{}^1$ - electron fluorine atom to give the MO as shown below.

MO - diagram of HF :



In this molecule NBO is the Non Bonding Orbital where the non bonded electrons are placed and the remaining electrons remain in AOs.

Thebonding molecular orbital is closer to the $2p_X$ - AO of the Fluorine atom.

Bond order.

In HF the number of electrons in BMO is 2 and that in the ABMO is ‘0’.

Therefore the bond order of HF = 1/2 (2-0)

= 1

Magnetic property of HF

As there is no unpaired electrons in any of MOs, this molecule is diamagnetic in nature.

Differences between VBT and MOT.

VBT	MOT
Only the half filled AOs of one atom combine with the half filled AO of the other atom.	All AOs whether half filled of completely filled overlap to give MOs.
It is based on the interaction between the individual atoms.	It is based on the interactions of nucleus of AOs.
According to VBT, wave property of atoms contribute to the total wave function.	In MOT, only the molecular orbital contribute to the total of wave function
VBT doesn’t explain the magnetic property of molecules.	This explains the magnetic property of the molecules.
Hybridisation plays an important role in VBT.	In MO hybridisation is given only lesser importance.

Similarities.

1. Method of filling up of electrons in the same in VBT and MOT.
2. The way of sharing electrons is the same in both methods.
3. During bond formation one AO must overlap the other AO.
4. The symmetry considerations in overlapping of orbitals is the same in VBT and in MOT.

4.1.3. COORDINATE BOND:

The bond in which, both the electrons needed for a covalent bond is supplied by only one atom is called the coordinate bond.

Explanation.

A coordinate bond is formed between two atoms, one of which has a complete octet and the other atom is short of two electrons. Hence the former atom supplies the pair of electron for the bond and the later one attains octet, by accepting the pair.

e.g.

$$H_3N :\!- + \quad BF_3 \longrightarrow H_3N \longrightarrow BF_3 \quad \text{(or)} \quad H_3N \; : BF_3$$

$$H_2O: \; + \; H^+ \longrightarrow [\, H_3O \,]^+$$

The atom that supplies the pair of electrons is called the donor and that which accept electrons is called the acceptor.

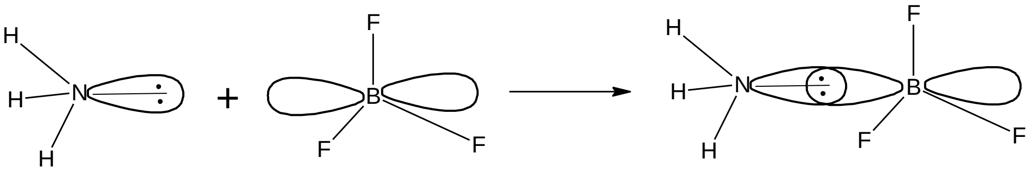
The coordinate bond is represented by an arrow mark, starting from the donor and ending at the acceptor.

Since only one atom donates a lone pair of electrons, this type of bonding is also called the dative bond.

As the coordinate bond is indistinguishable from covalent bond, it is also called the coordinate covalent bond.

According to orbital concept, and orbital containing alone pair overlaps with an empty orbital of the other atom.

For example, in Ammonia, one of the sp^3 - orbital with the lone pair of electrons overlap with the empty unhybridised orbital of Boran shown below.



CHARACTERISTICS:

1. Since the electrons in a coordinate bond are held firmly by the nuclei, the molecule doesn’t form ions in water.
2. Coordinate compounds are only sparingly soluble in water, where as most of them are freely soluble in organic solvents.
3. The rigid nature of this bond provides room for directional nature of the bond and hence for stereo isomerisms.
4. Since the electron pair is contributed by a single atom, the coordinate compound is semi polar in nature.
5. Therefore, physical properties lie in between electro valent and covalent compounds.

Importance of coordinate bond in the formation of metal complexes.

Co - ordinate compounds.

The addition compounds, which maintain their identity both in the solid state and in solution are called the complexes or coordination compounds.

e.g.

For example, K_2SO_4 . $Al_2(SO_4)3.24H_2O$ namely Potash alum when dissolved in water, dissociates in to small ions like, K^+, Al_3^+ and SO_4^{2-} ions.

But on the other hand $CuSO_4.4NH_3.H_2O$ namely Coper amine sulphate , when dissolved in water, dissociates as follows.

2+

$CuSO_4.4NH_3$ $CuH_2O(NH_3)4$ $+SO_4^{2-}$

Thus coordination compounds doesn’t give simple ions, instead give complex ions as indicated above.

Such compounds are called metal complexes or coordination compounds.

Importance of coordinate bonds.

Coordinate bonds play an important role in metal complexes. Werner showed that, the central metal atom of the complexes showed two types valencies.

1. One is primary valency. The primary valency is ionic valency just as in other ionic compounds and are non directional.

2. The second one is the secondary valency . The secondary valency important because,

a). It decides the number of ligands which are linked to the central metal atom. The secondary valency of a complex is given by the coordination number.

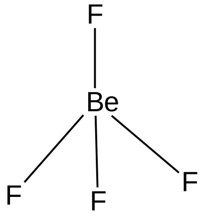
b). The secondary valency decides the geometry of the complexes. For example if the coordination number of the complex is four, then it has tetra hedral of square planar structure.

3. Very important use of it lie in the stereo chemistry of complexes.

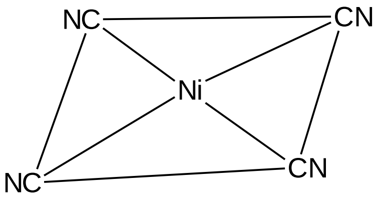
Since the secondary valency are directional in nature, the complexes have a particular shape. As a result of it, different isomers are possible for a particular complex. So they exhibit structural and stereo isomerism as shown below.

Structural isomerism.

For example coordination number four exhibits both tetra hedral and square planar geometry.

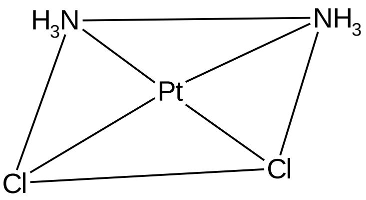


Tetrahedral

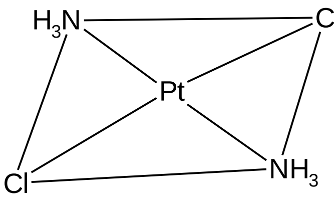


Square Planer

Geometrical isomerism.

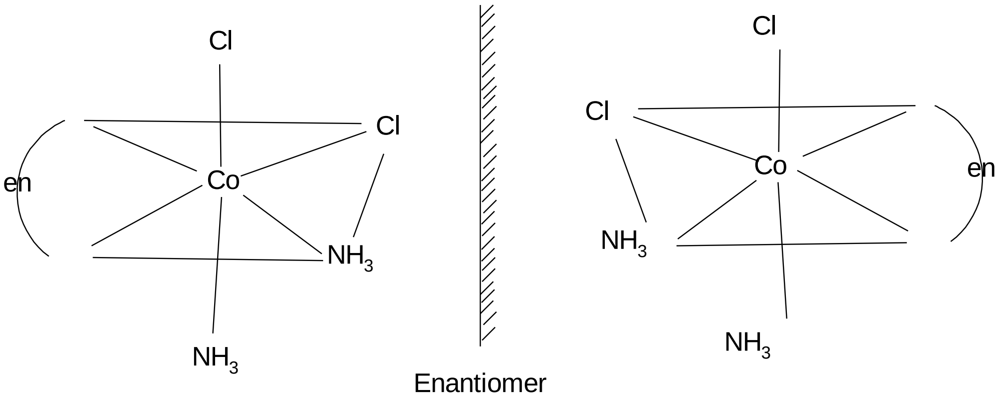


Cis - isomer



Trans - isomer

Stereo isomerism.



Enantiomer

4.2. HYDRIDES, CARBIDES AND NOBLE GASES:

4.2.1 HYDRIDES:

The compounds formed by the combination of Hydrogen with other elements, which have low electro negativity and more electro positivity as compared to Hydrogen are called the hydrides.

For example metals and non metals combine with hydrogen to give hydrides.

e.g.

NaH, CaH_2 , NH_3, PH_3

Classification.

Based on the physical and chemical properties, the Hydrides are classified in to the following four groups.

1. Ionic of salt like hydrides.

The hydrides formed by IA - and IIA - sub group elements, which have low electronegativity and more electro positivity as compared to H- atom are called the ionic hydrides.

e.g.

LiH, NaH, CaH_2

2. Covalent or molecular hydrides.

The hydrides formed by the III, IV, V, VI and VII - sub group elements are called the covalent or molecular hydrides.

e.g.

NH_3, SiH_4, AsH_3, H_2O, HCl, B_2H_6, CH_4

3. Metallic or interstitial hydrides.

Hydrides of ‘d’ block elements and Lanthanides and Actinides of ‘f’ block elements are called the metallic hydrides.

These hydrides are non stoichiometric and therefore known only very little.

e.g.

The most studied metallic hydride is UH_3.

4. Polymeric of intermediate hydrides.

Hydrides which don’t fit in to any of the above classification are called the polymeric of intermediate hydrides.

e.g.

$(BeH_2)n$, MgH_2, CuH, HgH_2

CHEMISTRY OF IONIC HYDRIDES:

LITHIUM HYDRIDE:

Preparation.

It is prepared by passing H_2 over heated Lithium. The reaction starts at 400^{o}c and is complete at 700^{o}c.

$$2\,Li + H_2 \qquad\qquad 2LiH$$

Physical properties.

It is white solids which melts at 680^{o}c. Since LiH is very small in size, it is not polarised but polarises H- ions so that, it has covalency.

But if electrolysed at temperatures slightly below its melting point, it liberates H_2 at the anode, indicating that it is a more an electrovalent compound.

It also conducts electricity.

Chemical properties.

1. Action on carbon monoxide.

It reduces CO to carbon.

$$LiH + CO \qquad\qquad LiOH + C$$

2. Action on water.

LiH reacts vigorously with water to liberate Hydrogen.

$$LiH + H_2O \qquad\qquad LiOH + H_2$$

3. Complex formation.

It reacts with Aluminium chloride in ether solution to give a complex hydride called Lithium Aluminium Hydride.

$$4LiH + AlCl3 \qquad\qquad Li[AlH_4] + 3Li$$

Uses.

1. Used as a strong reducing agent in synthetic organic chemistry.
2. Used in the preparation of LAH, which is a very good reducing agent.
3. Used in military as a source of H_2 in air and sea rescue balloons.
4. For making Boro hydrides which are used in jet propulsions.

SODIUM HYDRIDE:

Preparation.

Sodium hydride is prepared by passing pure and dry Hydrogen over sodium kept in Ni boat heated to 365^{o}c in a glass tube. After the reaction is over, colourless crystals of NaH is deposited on the upper cooler portion of the tube.

$2Na + H_2 \qquad\qquad 2NaH$

Properties.

Physical properties.

It is a colourless crystalline substance.

Chemical properties.

1 .Action of heat.

When heated above 330^{o}c, it decomposes to its elements.

$2NaH \qquad\qquad 2Na + H_2$

2. With water.

It is decomposed by water to liberate Hydrogen.

$NaH + H_2O \qquad\qquad NaOH + H_2$

3. Action of CO_2

Sodium hydride absorbs carbon dioxide to give Sodium formate.

NaH + CO2 $\qquad\qquad$ HCOONa

Sodium formate

4. Electrolysis.

Fused Sodium hydride on electrolysis liberates H_2 at the anode.

Uses.

1. Used as a reducing agent.
2. As a source of hydrogen.
3. For preparing Sodium formate.

CHEMISTRY OF COVALENT HYDRIDES:

SILANES:

Introduction

The hydrides of silicon with a general molecular formula SiH_{2n+2} where 'n' is number of Silicon atoms are called the Silanes.

If,

n = 1, we have mono Silane SiH_4 -------- Silomethane

n = 2, we have di Silane Si_2H_6 --------Siloethane

n = 3, we have tri Silane Si_3H_8 ----------Silo propane.

CHEMISTRY OF MONO SILANES:

Silo methane.

Preparation.

1. When Magnesium silicide is treated with dil. HCl taken in a flask in which air has been replaced by H_2, we get a spontaneous flow of Silane.

$$Mg_2Si + 4HCl \qquad 2MgCl_2 + SiH_4$$

2. It is also prepared by passing dry H_2, over hot silicon in an electric arc.

$$Si + 2H_2 \qquad SiH_4$$

3. More recently, mono Silane is prepared by reducing Silicon tetra chloride by LiH or NaH in ether solution at low temperature.

$$SiCl_4 + LiAlH_4 \qquad SiH_4 + LiCl + AlCl_3$$

$$Si_2Cl_6 + 6LiH \qquad Si_2H_6 + 6LiCl$$

$$Si_2Cl_8 + 8NaH \qquad Si_3H_8 + 8NaCl$$

Properties.

Physical properties.

It is colourless gas. Ignites in air and explode in Chlorine. Pure Silanes don't react withe dil. acids or water. If bubbled through water, as soon as comes in contact with air, each bubble ignites, giving vortex ring of finely divided Silica.

Chemical properties.

1. Action of heat.

When heated to red hot condition it decomposes to Si and H .

$$SiH \qquad Si + 2H$$

2. It is unstable and decomposes spontaneously on coming in contact with air.

$$SiH + 2O \qquad SiO + H O$$

3. With water.

When brought in to contact with water it slowly decomposes.

$$SiH + H O \qquad H SiO + 4H$$

4. With alkali.

It dissolves in strong alkali solution to give Silicates.

$$Si H + 2NaOH + 2H O \qquad Na SiO + 4H$$

5.Silane precipitate Silver from its salts.

$$4 AgNO + SiH \qquad Si + Ag + 2H SO$$

6. It give Copper silicide from Copper sulphate.

$$2CuSO + SiH \qquad Cu Si + 2H SO$$

DI SILANE or SILO ETHANE:

Preparation.

1. When Magnesium silicide is treated with HCl, di Silane is formed along withe Silomethane.

HCl

Mg Si SiH + Si H

2. It is better prepared by the action of Lithium silicide with strong HCl.

Li Si + 6HCl Si H + 6LiCl

di Silane

Properties.

Physical properties.

It is colourless liquid boiling at - 15^{o}c. Explodes with air. Stable at ordinary temperature and decomposes at 300^{o}c. Soluble in Carbon disulphide and Benzene.

Chemical properties.

1. With chloroform.

It reacts with Chloroform to give Carbon and liberates Hydrogen.

Si H + CHCl 2SiCi + HCl +2C + H

2. With CCl .

With Carbon tetra chloride it gives Carbon and liberates Hydrogen.

Si H + CCl 2SICl + 2C + 3H

3. With NaOH.

It reacts with Sodium hydroxide to give silicates.

Si H + 4NaOH + 2H O 2Na SiO + 7H

Differences between Silane and Alkane.

Silane	Alkane
Explode in Carbon tetra chloride Highly reactive. Reacts with water and Sodium hydroxide.	Does not explode. Low reactive Does not rear with water and Sodium hydroxide.

Act as a strong reducing agent	Not a reducing agent
Tri Silylamine is not a base	Tri methylamine is base.

Reasons for difference.

The reason for this difference in chemical behaviour can be explained as follows.

1. Electro negativity.

The electronegativity values of C, Si and H - are as follows.

$$C = 2.5 ; \quad Si = 1.8; \quad H = 2.1$$

Form these values it is clear that, carbon atom attains a partial -ve charge where as Si acquires a partial +ve charge when bonded to the Hydrogen atom. Therefore nucleophilic attack is easier on Silicon.

2. Size of the atoms.

The larger size of Silicon makes it easy for the attacking agent to approach it and hence more reactive.

3. Electronic configuration.

Silicon has low energy ‘d’ orbital which are used for the formation of intermediate, with lower activation energy. so Silanes are more reactive than the alakanes.

METALLIC HYDRIDES:

Uranium hydride.

Among the metallic hydrides Uranium hydride is the most studied.

Preparation.

Uranium reacts with Hydrogen at 25^{o}c to give Uranium hydride as a black pyrophoric powder.

$$2U + 3H \qquad 2UH$$

$$250^{o}c$$

Properties.

Physical properties.

Like the metal it conducts electricity. Chemically very reactive and inflames in air. Therefore it is more suitable than the metal for preparing various compounds of Uranium.

Chemical properties.

1. With Oxygen.

It reacts with Oxygen to give Uranium octa oxide.

6UH + 8O   2U O + 9H

2. With water.

It reacts with water to give Uranium oxide.

2UH + 4H O   2UO + 4H

Similarly it reacts with Hydrogen sulphide to give Uranium sulphide.

2UH + 4H S   2US + 4H

3. With Bromine.

With Bromine it give Bromine tetrabromide.

2UH + 4 Br   2UBr + 3H

4. With HF and HBr it reacts as follows to give the corresponding halides.

2UH + 8HF   2UF + 7H

2UH + 3HCl   UCl + 7H

2UH + 3HBr   UBr + 7H

COMPLEX HYDRIDES:

Lithium Aluminium Hydride [LAH]:

Preparation.

1. It is prepared by action of LiH with anhydrous Aluminium chloride in ether.

4LiH + AlCl   LiAlH + LiCl

2. Large scale preparation.

a). On industrial scale, LAH can be prepared by direct combination of the constituent elements under high pressure in presence of ether.

ether

Li + Al + 2H LiAlH

150^{o}c, 150atm.

b). Preferably it can be prepared from Sodium Aluminium hydride Which can be prepared by combining the constituent elements as follows.

Na + Al + 2H NaAlH

NaAlH + LiCl LiAlH + NaCl

Properties.

Physical properties.

It is white non volatile crystalline solid. Freely soluble in ether but with water it vigorously reacts.

Chemical properties.

1. With water.

Water and Ethanol attacks LAH readily to liberate Hydrogen.

LiAlH + 4H O LiOH + Al(OH) + 2H

LiALH + 3EtOH Li[AlH(OEt)] + 3H

Lithium Aluminium ethoxide

2. Similarly it reacts with the following compounds to liberate hydrogen.

$$LiAlH_4 + 3C_2H_2 \rightarrow Li\left[Al\left(CH = CH_2\right)_2\right] + 2H_2$$

$$LiAlH_4 + 4NH_3 \rightarrow Li\left[Al\left(NH\right)_2\right]_4 + 4H_2$$

$$LiAlH_4 + 4PH_3 \rightarrow Li\left[Al\left(PH_2\right)_4\right] + 4H_2$$

$$LiAlH_4 + 4RN_2 \rightarrow Li\left[Al\left(HNR\right)_4\right] + 4H_2$$

$$LiAlH_4 + Me_3N \rightarrow \left(Me_3\right) N\,AlH_3 + LiH$$

3. As a reducing agent.

It reduces a number of inorganic compounds as follows.

$BCl_3 \xrightarrow{LAH} B_2H_6$

Diborane

$PCl_3 \xrightarrow{LAH} PH_3$

Phosphine

$SiCl_4 \xrightarrow{LAH} SiH_4$

Silane

4. Reduction of organic compounds.

It reduces carbonyl compounds to alcohols without affecting the carbon - carhon double bonds.

$$CH_3CHO \xrightarrow{LAH} CH_3CH_2OH$$
$$CH_3COCH_3 \xrightarrow{LAH} CH_3CHOCH_3$$
$$CH_3CH = CHCHO \xrightarrow{LAH} CH_3CH = CH_2CHOH$$

Uses:

1. It is used as a very good reducing agent for many organic and inorganic compounds.

2. It reduces carbonyl compounds without affecting the carbon - carbon double bonds.

But it can’t be used in the aqueous media, because it reacts vigorously with water where as Sodium boro hydride is not affected by water.

CARBIDES:

Compounds of carbon with a less electro negative elements, is called the carbides.

e.g.

CaC_2 ; Al_4C_3 ; Mg_2C_2

Chemistry of Calcium carbide.

Preparation.

It is prepared by heating strongly lime and coke.

$$CaO + 3C \xrightarrow{2200^{o}c} CaC + CO$$

Properties.

Physical properties.

It is a hard crystalline solid. The pure solid is white in colour but the commercial sample is usually grey.

Chemical properties.

1. With water.

It reacts with water to give Acetylene.

$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$$

2. With Nitrogen.

It reacts with Nitrogen at 1100°c, to give Calcium cyanamide.

$$CaC_2 + N_2 \xrightarrow{1100^{o}c} \underset{\text{Calcium cyanamide}}{CaNCN} + C$$

Uses:

1. It was used as major source of acetylene which was largely used in oxy - acetylene flames for welding purposes.

2. It is the important chemical intermediate in the manufacture of Calcium cyanamide, which is used as a fertilizer.

3. Used in the manufacture of Urea, a fertilizer.

4. Used in production of Malanine.

Carbides which yield acetylene are called the acetylides.

Aluminium carbide. Al C

Preparation.

When Al - is heated strongly with coke, we get Aluminium carbide.

$$3Al + 4C \longrightarrow Al_4C_3$$

Aluminium carbide

Properties.

Physical properties.

It exists as a transparent crystal and non conductor of electricity in the solid state.

Chemical properties.

Aluminium carbide reacts with water to give Methane.

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH) + 3CH_4$$

Methane

Carbides which gives Methane during hydrolysis are called the methanides.

Magnesium carbide

It is prepare by heating Magnesium with Coke.

$$2Mg + 3C \xrightarrow{\Delta} Mg_3C_2$$

Magnesium carbide

Magnesium carbide reacts with water to give Allylene.

$$Mg_3C_2 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3C \equiv CH$$

Allylene

These type of carbides which yield allylene are called the allylides.

Silicon carbide.

It is prepared by heating quartz or sand with an excess of coke in an electric furnace at 2000 - 2500^{o}c.

$$SiO + 2C \xrightarrow[2000-2500^{\circ}c]{\text{electric arc}} SiC + Co$$

Silicon carbides

Properties.

Physical properties.

It is very often dark purple in colour and very unreactive.

Chemical properties.

It is not affected by acids except Phosphoric acid but affected by alkalis like NaOH in air to give Silicate.

$$SiC + 2NaOH + 2O_2 \longrightarrow Na_2 SiO_3 + CO_2 + H_2 O$$

With Chlorine it gives Silicon tetra chloride.

$$SiC + 2Cl_2 \longrightarrow SiCl_4 + C$$

Uses.

1. Tones and tones of Silicon carbide is used in the name of Carborundum as an abrasive.
2. It is used as shield from radiations.

4.2.3 NOBLE GASES:

The elements of group ‘0’ (Group - 18) ,which are inert or reluctant to react are called the ‘Noble gases’ or inert gases.

These are the least reactive metals in the periodic table. They are, He, Ne, Ar, Kr, Xe and Rn.

Position in the periodic table.

Even though Mandeleaf had left spaces in the periodic table for several elements which were not known at that time, he had not left any blank space for noble gases.

It was because, Mandeleaf’s classification of elements was based on the chemical properties of elements and therefore there was no chance to recognise the noble gases, which had no chemical reactivity.

Only after Ramsay’s discovery of these gases, a new group was introduced in the periodic table called the ‘zero group’ specifying their zero valency.

The reason for placing these elements in the ‘0’ group is as follows.

1. 1. These elements have ns np electronic configuration. This is a stable configuration and so they are inert in nature.
2. They have zero electron affinity and very high ionisation potentials. Their ionisation energies are higher than any other element in the periodic table.
3. Under normal conditions, they have little tendency to form bonds. Therefore they exist in mono atomic state.
4. Therefore as per the atomic number and the number of valencies of these elements, they are placed in zero group, which lies between the most electro negative group - VII halogens and the most electro positive group - I alkali metals.

COMPOUNDS OF XENON:

Xenon di fluoride.

Preparation.

1. It is best prepared by heating a mixture of Xe and Fluorine in a 2:1 molecular ratio at 400^{o}c in a Ni tube.

$$Xe + F_2 \xrightarrow[400^0 C]{Ni} XeF_2$$

Xenon difluoride

It can also prepared by subjecting an electric discharge through a 1:1 mixture of constituent elements.

$$Xe + F_2 \xrightarrow{electic\,discharge} XeF_2$$

2. Photo chemical combination of Xe and Fluorine under Mercury vapour gives Xenon difluoride.

$$Xe + F_2 \xrightarrow{Hg-vapour} XeF_2$$

3. By the fluorination of Xe by oxygen monofluoride at -178^{o}c also we can prepare this compound.

$$Xe + O_2F_2 \xrightarrow{-178^0 C} XeF_2 + O_2$$

Properties.

Physical properties.

It is a colourless crystalline solid which melts at 140^{o}c. Dissolves in HF without reacting with it.

Chemical properties.

1. It reacts with Hydrogen to give Hydrogen fluoride.

$XeF + H \quad Xe + 2HF$

2. With water it liberates Oxygen

$Xe F + 2H O \quad 2Xe + 4HF + O$

3. It oxidises Iodine to IF in presence of Boron trifluoride.

$XeF + I \quad 2IF + Xe$

4. It reacts with HCl to liberate chlorine.

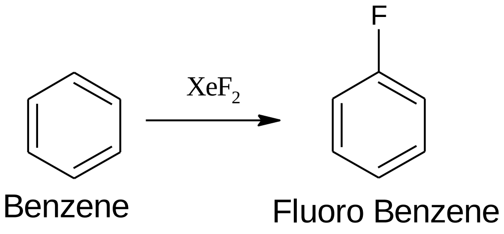
$XeF + 2HCl \quad Xe + 2HF + Cl$

5. It reacts with sulphur trioxide to give Sulphur hexa oxy fluoride.

$XeF + 2SO \quad Xe + S O F$

6. As a fluorinating agent.

Being a mild fluorinating agent, it fluorinates Benzene in to fluoro benzene.



Structure and shape of Xenon di fluoride.

Normally in molecules not having double bonds, the number of orbitals of the central atom required for hybridisation is calculated from the valence shell electrons present around the central atom.

In xenon fluoride, since each F - atom contribute one electron, the total number of electrons around the central atom namely Xenon,

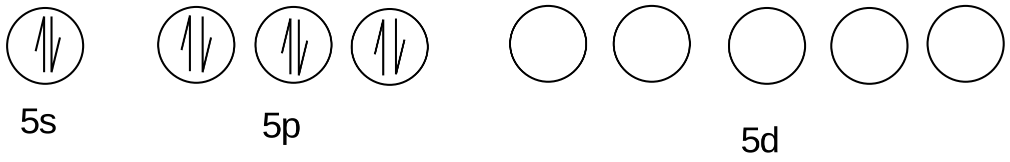
$= 8 + 2$

$= 10$

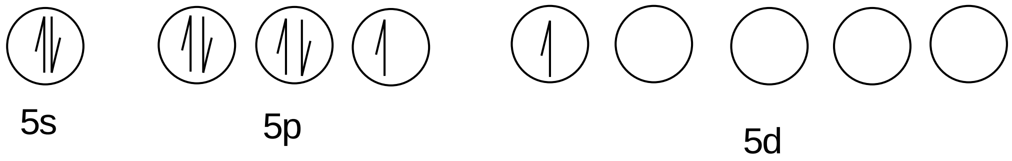
Therefore the number of orbitals of Xe, taking part in hybridisation must be equal to ‘5’ orbitals.

Therefore one of the 5p - electrons must be exited to one of the 5d - orbitals as shown below.

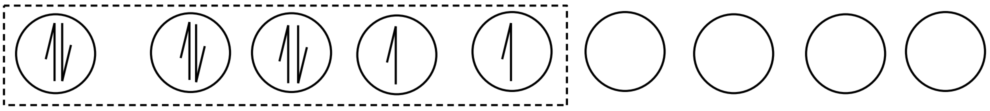
The electronic configuration of Xe in the ground state is



The exited state configuration will be,

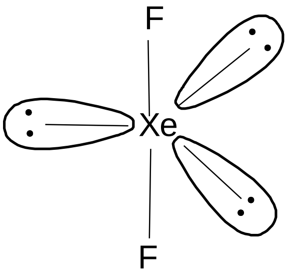


Now one 5s - three 5p- and one 5d - orbital hybridise as shown below to give a sp d - hybridised orbital.



All the hybridised orbitals are equal. Now two of the singly filled sp3 d orbitals overlap with the half filled 2p - orbital of two F - atom to give two Xe - F sigma bonds.

As a result Xenon difluoride has a trigonal bi pyramidal structure having the lone pairs in the three equatorial positions and two Fluorine atoms occupying the apex positions as shown below.



Xenon tetra fluoride.

Preparation.

1. By passing a mixture of Xe and F - in a molecular ratio of 1:5 through a Nickel tube at 400 under 5 - 6 atmosphere pressure.

Xe + 2F XeF

Xenon tetra fluoride

2. A 1:1 ration of Xe and F when passed through an electric discharge at - 80^{o} c gives XeF .

$$Xe + 2F_2 \xrightarrow{\text{electric discharge}} XeF_4$$

Properties.

Physical properties.

It is colourless crystalline solid which melts at 117.1 . It sublimes readily. Dissolves in HF without reacting.

Chemical properties.

1. Reduction.

It is reduced by hydrogen to the element.

$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF$$

2. It undergoes disproportionation in water to give a highly explosive compound, Xenon trioxide.

$$2XeF_4 + 3H_2O \longrightarrow Xe + XeO_3 + 6HF + F_2$$

But if the reaction is carried out at -80^{o}c , it forms xenon oxy fluoride.

$$XeF_4 + H_2O \xrightarrow{-80^{o}C} XeOF_2 + 2HF$$

Xenon oxy fluoride

3. It reacts with BCl to give BF .

$$XeF_4 + 4BCl_3 \longrightarrow 4BF_3 + 3Xe + 6Cl_2$$

4. Fluorination.

It being a strong fluorinating agent than XeF , undergoes following fluorination reactions.

$$XeF_4 + 2Hg \longrightarrow Xe + 2HgF_2$$
$$XeF_4 + Pt \longrightarrow Xe + PtF_4$$
$$XeF_4 + 2SF \longrightarrow Xe + \underset{\text{sulphur hexa fluoride}}{2SF_6}$$

5. Addition reaction.

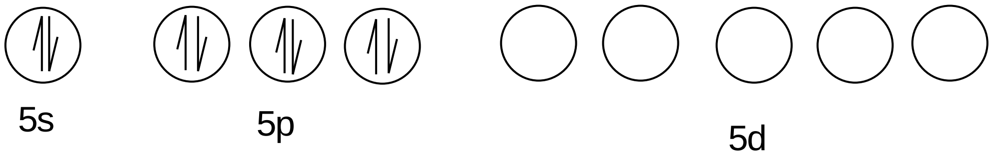
It forms an addition compound with Antimony penta sulphide.

$$XeF_4 + SbS_5 \longrightarrow \underset{\text{Addition compound}}{XeF_4.SbS_5}$$

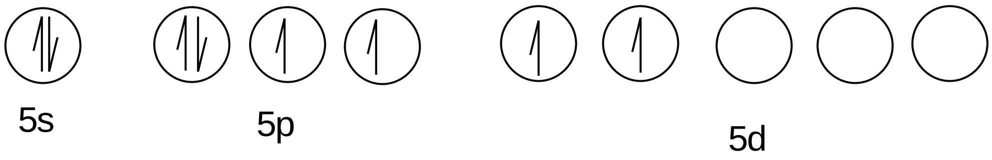
Shapes of Xenon tetra fluoride.

In xenon tetra fluoride, two 5p - electrons are exited to two 6d - orbital as shown below.

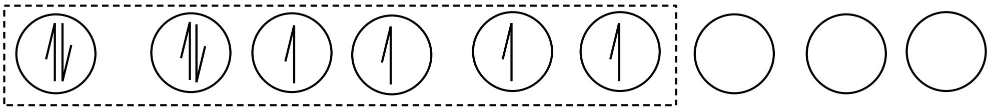
Electronic configuration in the ground state is,



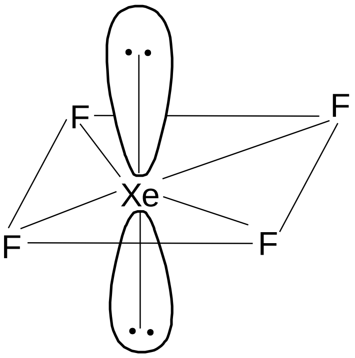
In the exited state the electronic conflagration will be,



The hybridisation taking place in this molecule is sp d as shown below



Though the compound must be octa hedral according to orbital hybridisation, Valence shell electron pair repulsion makes it a square planar compound as shown below with two lone pair of electrons pointing towards the apex.



Xenon hexa fluoride. XeF

Preparation.

1. By heating Xe with excess of Fluorine in the ratio of 1:20 in a Nickel vessel at 25 - 300 at 50 atmosphere, we can prepare Xenon hexa fluoride.

$$Xe + 3F \longrightarrow XeF$$

2. It can also be prepared by passing an electric discharge through a 1:3 mixture of Xenon and Fluorine.

$$Xe + 3F \longrightarrow XeF$$

3. XeF_6 is obtained when XeF_4 is allowed to react with F_2 .

$$XeF_4 + F_2 \longrightarrow XeF_6$$

Properties.

Physical properties.

It is a white crystalline solid melting at 49.5 . Most volatile of all the Xenon fluorides, with greenish yellow vapour. It is extremely reactive.

Chemical properties.

1. It dissolves in HF to give the following ionic compound, which is a good conductor of heat and electricity.

$$XeF_6 + HF \longrightarrow XeF_5 + HF_2$$

2. Reduction.

It reduced to Xe by Hydrogen, Ammonia and HCl.

$$XeF_4 + 3H_2 \longrightarrow Xe + 6HF$$

$XeF_4 + 8NH_3 \longrightarrow Xe + 6NH_4\ F + N_2$

$XeF_4 + 6HCl \longrightarrow Xe + 6HF + 3Cl_2$

3. Hydrolysis.

It undergoes slow hydrolysis with moisture in the atmosphere to give the explosive called Xenon trioxide.

$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

Xenon trioxide

4. With glass or quartz, it undergoes a sequence of reactions to give Xenon trioxide.

$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$

$2XeOF_4 + SiO_2 \longrightarrow 2XeO_2\ F_2 + SiF_4$

$2XeO_2\ F_2 + SiO_2 \longrightarrow 2XeO_3 + SiF_3$

Since the final product XeO obtained is a dangerous explosive, XeF can't be stored in a glass or quartz vessels.

5. Formation of adducts.

It reacts with Fluorine acceptors to give adducts.

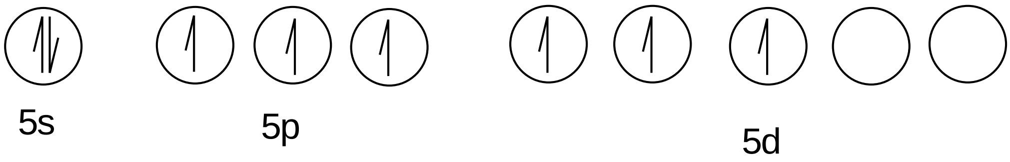
$XeF_6 + SbF \longrightarrow XeF_6 . SbF_5$ or $[XeF_5\ ]\ [SbF_6\ ]$

$XeF_6 + AsF_5 \longrightarrow XeF_6 . AsF_5$ or $[XeF_5\ ]\ [AsF_6\ ]$

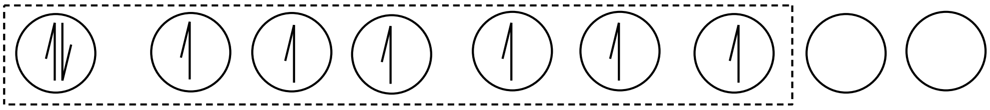
Shape of Xenon hexa fluoride.

Three electrons from 5p - orbital of Xenon is exited to the 5d - orbital to give a total of six unpaired electrons in the outer most orbital as shown below.

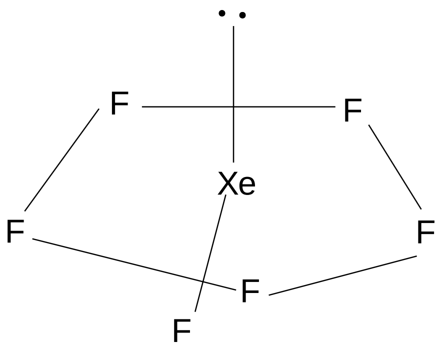
Exited state electronic configuration.



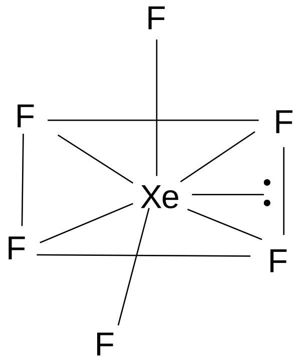
A total of seven orbitals namely one s - orbital, three p - orbitals and three d - orbitals hybridise to give a sp d - hybridised orbital as shown below.



Therefore Xenon hexa fluoride must be in pentagonal bi pyramidal shape as shown.



But it is perfectly believed to have a distorted hexagonal structure, in which all the six fluorine atoms occupy six corners and the lone pair is present at the centre of one of the triangular faces as shown.



Xenon octa fluoride. XeF

Preparation.

When Xe is allowed to react with large excess of Fluorine, under pressure, a small amount of XeF is formed.

$$Xe + 4F_2 \longrightarrow XeF_8$$

This compound is not studied well and the structure is also not known.

Xenon oxy di fluoride. $XeOF_2$.

Preparation.

It is prepared by slow and partial hydrolysis of XeF , at low temperature.

$$XeF_4 + H_2O \xrightarrow{-80^{o}C} XeOF_2$$

It is not a very stable molecule.

Xenon oxy tetra fluoride. $XeOF_4$

Preparation

1. By the partial hydrolysis of XeF we can prepare a small quantity of Xenon oxy tetra fluoride.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

2. By heating a mixture of Xe and F in the ratio of 1 : 4 in presence of large excess of O at 230 , we can prepare an appreciable quantity of XeOF .

$$Xe + 2F_2 \xrightarrow[230^{o}C]{O_2} XeOF_4$$

Properties

Physical properties

It is colourless compound which melts at -46

Chemical properties.

1. It is reduced by hydrogen to the element.

$$XeOF_4 + 3H_2 \longrightarrow Xe + H_2O + 4HF$$

2. It reacts with water to form another oxy fluoride called Xenon di oxy di fluoride.

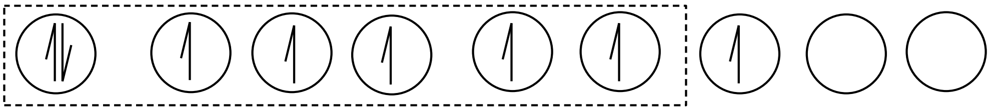
$$XeOF_4 + H_2O \longrightarrow XeO_2F_2 + 2HF$$

3. With Silica, it gives Xenon dioxy difluoride.

$$2XeOF_4 + SiO_2 \longrightarrow XeO_2F_2 + 2HF$$

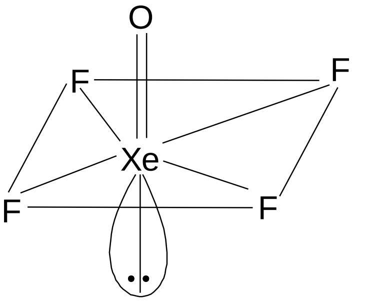
Shape of the molecule.

The hybridisation in this molecule was found to be sp d - as shown.



sp3 d2 - hybridisation

Therefore this molecule has a square pyramid structure with oxygen having a double bond with Xenon as shown below.



Xenon dioxy difluoride. Xe O F

Preparation.

Partial hydrolysis of XeOF yields Xenon dioxy difluoride.

$XeOF_4 + 4H_2O \longrightarrow XeO_2F_2 + 2HF$

2. In a similar way XeOF on treatment withe silica yields Xenon dioxy difluoride.

$XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$

Properties

Colourless solid. Melts at 30.8 .

Easily hydrolysed to Xenon trioxide.

$XeO_2\ F_2 + H_2O \longrightarrow XeO_3 + 2HF$

Structure.

The central atom namely Xenon is sp d - hybridised and therefore has trigonal bipyramidal shape.

Xenon tri oxide.

Preparation. XeO

1. When Xenon tetra fluoride is hydrolysed, Xenon trioxide is formed in small quantities.

$2XeF_4 + 3H_2\ O \longrightarrow Xe + XeO_3 + 6HF + F_2$

2. Xenon hexa fluoride when kept in moisture yields Xenon trioxide.

$XeF_6 + 3H_2\ O \longrightarrow XeO_3 + 6HF$

Properties.

Physical properties.

It is a white non volatile compound and soluble in water. It explodes like TNT when dry.

Chemical properties.

1. As an oxidising agent.

It acts as powerful oxidising agent and oxidises Plutonium ion in to its higher oxidation state.

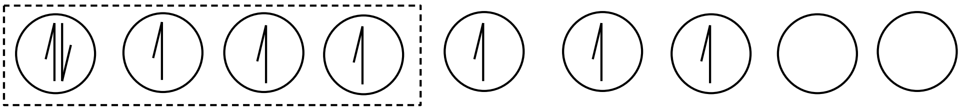
$$6Pu^{2+} + XeO_3 + 6H^+ \longrightarrow 6Pu^{4+} + Xe + 3H_2O$$

2. In aqueous NaOH it disproportionates as follows.

$$2XeO_3 + 4NaOH + 6H_2O \longrightarrow Xe + O_2 + Na_4XeO_6 .8H_2O$$

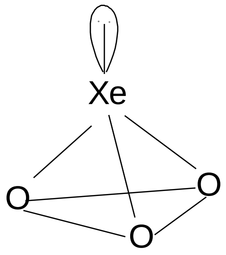
Shape of the molecule.

The central atom namely Xenon is believed to be sp - hybridised in the exited state as shown below.



sp - hybridisation

Therefore the molecule has a tetra hydral shape with the lone pair of electrons in one corner.



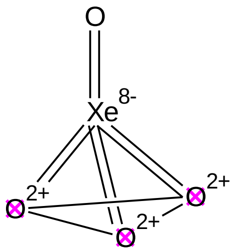
Xenon tetroxide. XeO

Preparation.

It can be prepared by treating Barium per xenate with anhydrous Sulphuric acid as follows.

$$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + BaSO_4 + 2H_2O$$

It is not as stable as the trioxide and has a tetra hedral structure as shown below.



Questions for exercise.

1. 1. Give the MO diagram or Hydrogen molecule ion H and calculate the bond order.
2. Give the MO electronic configuration of F molecule.
3. Which of NO and N is more stable on the basis of bond order.
4. 4. Explain the orbital overlap in the formation of H O ion by coordinate bond.
5. Explain the formation of ionic bond in Magnesium sulphide molecule.
6. Calculate the bond order of Ne molecule on the basis of the electronic configuration of its MO.

NOTES

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

UNIT – V

INTRODUCTION:

Unit - V deals mainly with the behaviour of ideal and real gases. As for as ideal gas is concerned, the gas laws, kinetic theory of gases, derivation of gas laws from the kinetic theory and their deviation from ideal behaviour are discussed in detail.

In the second portion of the topic the reason for deviation and the correction to the postulates of kinetic theory of gases and Virial equation come important for discussion.

In the second part of the unit, Liquid state, structure of liquids and their important properties like viscosity refractive index etc. are discussed. Finally physical properties like molar volume, parachor, viscosity and molar volume and their chemical constitution are discussed in full detail.

UNIT - V

THE GASEOUS STATE

5.1.1 BEHAVIOUR OF IDEAL GASES:

Introduction.

All maters, which are made up of molecules in the universe exist in three states namely, solid, liquid and gaseous.

Out of these three states, the gaseous state is the simplest and uniform in its behaviour. For example, irrespective of their colours, odor or chemical nature, all of these have the following characteristic properties.

1. Indefinite dispensability.

All gases expand indefinitely and fill any vessel, no matter bow it is large in which the gas is placed.

2. Compressibility.

They can be compressed easily.

3. Diffusion.

They intermix with other gases and move in to empty space without any difficulty.

4. Homogeneity.

Individual gas of a mixture is completely homogeneous.

5. Low density.

Gases possess relatively low density.

6. Pressure.

All gases exerts a pressure in the walls of the container.

GAS LAWS:

The behaviour of gases, when the external conditions like temperature and pressure are varied, are independent of the nature of the gas. That is all of them have almost same behaviour and these behaviours are explained by some generalisations called GAS LAWS which are discussed in detail one by one as follows.

1. BOYLE'S LAW:

Boyle's law states that, at constant temperature the volume of a definite mass of a gas is inversely proportional to its pressure.

If V = volume the gas,

P = pressure of the gas,

T = temperature of the gas and

n = the number of molecules of the gas

then mathematically,

$$V \alpha \frac{1}{P}$$

or $PV = k$ (k = constant)

Since the value of PV is a constant for all gases,

$P_1 V_1 = P_2 V_2 = k$

where P_1 and V_1 stands for gas one P_2 V_2 stands for the gas two.

2. CHARLES'S LAW : or

GAYLUSSAC'S LAW.

The law states that, at constant pressure, the volume of any gas is directly proportional to its absolute temperature.

That is, the volume of any gas at constant pressure expands by the same fraction of its at 'o'k, for every 1k raise of temperature.

If V = volume of the gas,

T = the temperature of the gas and

P = the pressure of the gas

then, mathematically, $V \alpha T$

or $\frac{V}{T}$ = Constant

AVAGADRO'S LAW:

The law states that, equal volume of all gases at the same conditions of temperature and pressure, contain the same number of molecules.

If V = volume of the gas,

n = the amount of the substance

and P and T are constant,

then mathematically the law is ,

$$V \alpha T$$

IDEAL GAS LAW or GAS EQUATION:

The general gas equation was arrived by combining both the Boyle's law and the Charles's law as follows.

Let us say that , at temperature T_1

V_1 is the volume of the gas and

P_1 is the pressure of gas

at temperature T_2

V_2 is the volume of the gas and

P_2 is the pressure of the gas.

Now let us assume that, at temperature T_1 ,

the volume raises to V

and pressure raises to P_2 .

Therefore according to Boyle's law the temperature being constant,

$$V \alpha \frac{1}{P_2}$$

i.e. $P_2 V$ = constant and

since $V_1 \alpha \frac{1}{P_1}$

$$P_2 V = P_1 V_1$$

$$\text{or } V = \frac{P_1 V_1}{P_2} \to (1)$$

Secondly let us assume that, the volume at V at T_1 raises to V_2 at temperature T_2 .

As per Charles's law,

$$V \alpha T_1$$

or $$\frac{V}{T_1} = \text{ a constant}$$

and since $V \alpha T_2$

$$\frac{V_2}{T_2} = \text{ a constant}$$

$$\therefore \frac{V}{T_1} = \frac{V_2}{T_2}$$

$$\therefore V = \frac{V_2 T_1}{T_2} \qquad \rightarrow (2)$$

Substituting equation 2 in 1 we get

$$\frac{V_2 T_1}{T_2} = \frac{P_1 V_2}{P_2} \quad \rightarrow (3)$$

after cross multiplication of the equation 3 it becomes,

$$P_1 \; V_1 \; T_2 \quad = \quad P_2 \; V_2 \; T_1$$

or $$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = \text{ constant.}$$

$$\frac{PV}{T} = k = \text{constant}$$

Thus it is clear that, the value of 'k' depends on the amount of gas and the units of pressure and temperature.

But we know that, according to Avagadro's law, if the quantity of the gas is fixed as 1 - mole at a given temperature and pressure, the volume of all gases will be the same.

Therefore for one mole of any gas, $\frac{PV}{T}$ must have the same value, which is represented by 'R' and hence the equation takes the form,

$$\frac{PV}{T} = R$$

$$\text{or} \quad PV = RT \quad \text{--------------------} \quad 4$$

Were ‘R’ is the molar gas constant and the equation 4 is called the ideal gas equation.

For ‘n’ molecules of the gas the equation can be written as ,

$$PV = nRT$$

NUMERICAL VALUE OF ‘n’ :

At standard conditions of temperature and pressure (at STP),

T = 273 . 16k ;

P = 1 atmosphere or 1.0132 X 10 dyne the

volume of the gas is = 22 . 4 liters or dm and

n = 1 mole.

The ideal gas equation is

$PV = nRT$

$$\text{or} \quad R = \frac{PV}{nT}$$

Substituting the values we get,

$$R = \frac{1.0132 \times 10^{5} \times 22.413 \times 10^{-3}}{1.0 \times 273.16}$$

$R = 8.314 Jk^{-1} mol^{-1}$

DALTON’S LAW OF PARTIAL PRESSURE :

The relationship between the total pressure and the pressure of constituent gases of mixture, was explained be J. Dalton in the form of a law called “ the law of partial pressures” .

The law states that, the total pressure of a mixture of gases is equal to the sum of the partial pressures of constituent gases.

Let, P denotes the total pressure of a mixture of gases and P ,

P and P ...... represents the partial pressures to the gases 1, 2, 3, and so on, if they alone occupy the same volume respectively, then as per the law,

$$P + P_1 + P_2 + P_3 + ...$$

This law is obeyed by ideal gases only.

Use of this law.

This law can be used to calculate the actual pressure of individual gases collected over water at constant temperature.

GRAHAM'S LAW OF DIFFUSION :

The law states that," the rate of diffusion of a gas is inversely proportional to the square root of its density ".

If = the rate of diffusion,

D = the density and

k = is a constant,

then mathematically the law is,

$$\gamma \ \alpha \ \frac{1}{\sqrt{D}}$$

Use

1. It is used for the determination of vapour density

2. For the determination of molecular weight.

KINETIC MOLECULAR THEORY OF GASES: or

KINETIC THEORY OF GASES

Kinetic theory was first put forward by Robert Hook, to explain the general behaviour of gases, provided by experiments. This theory was then developed by others and the present one is that of Maxwell and Boltzmann.

The postulates of kinetic theory.

1. Gases consists of minute particles called molecules which are in perpetual motion and collide with each other.

2. Molecules are moving very fast in straight lines at random speed and direction.

3. There are no force of attraction between the molecules and between the molecules and the vessel.

4. The molecular motions are perfectly elastic so that there is no loss or gain in kinetic energy in each collision although there may be exchange of energy between the particles during collision.

5. Though the kinetic energy of the molecules are different, the average kinetic energy is a constant and is directionally proportional to the absolute temperature.

6. The effect of gravity is negligible, as compared to the effect of continued collision.

7. The actual volume of the molecules is negligible, as compared to the total volume of the gas or the container.

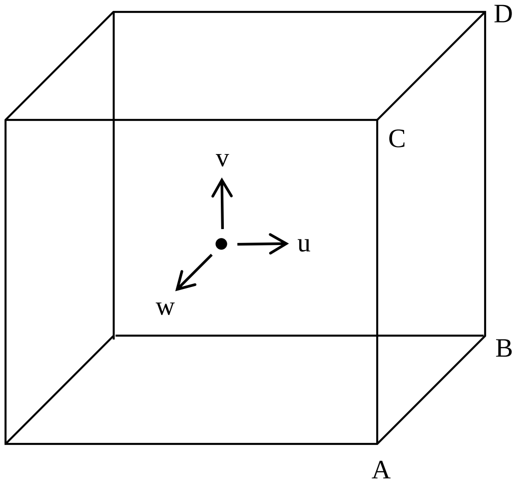
8. The pressure is due to the bombardment of the molecules on the walls of the vessel.

It is very important to note that, the above postulates are meant for an ideal gas only and only approximately valid for real gases.

DERIVATION OF KINETIC GAS EQUATION:

Consider a gas of ‘n’ molecules with a mass of ‘m’ grams contained in a cubic vessel whose sides are of length ‘l’.

Let the average velocity or speed of the molecule be ‘c’ cm. per second. Since the molecules are actually moving in zig zag manner, the average velocity can be resolved into three components namely u, v and w in three mutually perpendicular directions as represented below.



These three component velocities can be related to the average velocity by the equation,

$$c = u + v + w$$

Since the molecules are free to move in any direction, we can assume that ,

$c = u = v = w$

$c = u = u = u$

i.e $c = 3u$

or $u = 1/3c$

where ‘u’ is the mean velocity.

Now consider a single molecule moving perpendicular to the face ABCD with velocity ‘u’.

Now its momentum = mu

After striking the face ABCD, it will return with same speed but in the opposite direction.

Therefore the momentum is = - mu.

The change in momentum = mu - (- mu)

i.e mu + mu = 2mu.

Therefore the change in momentum, of ‘n’ molecules for one direction,

= 2mun

We know that the average speed towards the direction of the face ABCD is

= u cm. /sec.

and let the length of the sides of the cube be ‘l’.

Therefore the number of collisions per second on the side ABCD only is

= u/2l (since it has to travel 2l cm every time to collide on ABCD)

The total momentum for u/2l collisions of ‘n’ molecules,

$$= 2mnu \times \frac{u}{2l}$$

$$= \frac{mnu^2}{l}$$

But it is known that, $u^2 = \frac{c^2}{3}$

The total change in momentum $= \frac{1}{3} \times \frac{mnc^2}{1}$

Since pressure is equal to force per unit area,

The total pressure on one side 'p' $= \frac{1}{3} \times \frac{mnc^2}{l \times l^2}$

$$\text{i.e. } p = \frac{1}{3} \times \frac{mnc^2}{l^3}$$

$$= = \frac{1}{3} \times \frac{mnc^2}{V} \quad (\text{since } l^3 = v)$$

$$pv = \frac{1}{3} mnc^2$$

This is known as the kinetic gas equations.

Derivation of Boyle's law from kinetic gas equation.

Boltzman showed that, the kinetic energy of 'n' moving particles is,

$$KE = \frac{1}{2} mnc^2 = \text{a constant}$$

From kinetic theory of gases we have,

$$PV = \frac{1}{3} mnc^2 \qquad \text{----------------} \quad 1$$

After multiplying and dividing the equation - 1 by '2'

We get,

$$PV = \frac{2}{2} \times \frac{1}{3} mnc^2$$

$$= \frac{2}{3} \times \frac{1}{2} mnc^2$$

But according to Boltzmann, at constant temperature,

$$= \frac{1}{2} mnc^2 \text{ is a constant.}$$

$$PV = \frac{2}{3} \times \text{ constant (since 1/2mnc is a constant)}$$

$PV = \text{a constant}$.

Hence the Boyle's law.

Derivation of Charles's law from kinetic equation.

We know that according to kinetic theory of gases,

$$PV = \frac{1}{3}mnc^2$$

After doing some manipulation the equation becomes,

$$PV = \frac{2}{2} \times \frac{1}{3}mnc^2 \quad (1/2mnc^2 = KE = \text{constant})$$

It is known that the total kinetic energy 1/2 mnc increases with temperature.

i.e $1/2\ mnc^2$ absolute temperature.

PV is also αT

If P is a constant, then $V \ \alpha T$

That is the volume of a given mass of a gas is proportional to T which is the Charles's law.

Avogadro's law.

Consider equal volumes two gases at STP. Therefore according to kinetic theory ,

$$P_1V_1 = \frac{2}{3} \times \frac{1}{2} m_1^2 n_1^2 c_1^2$$

$$P_2V_2 = \frac{2}{3} \times \frac{1}{2} m_2^2 n_2^2 c_2^2$$

If P and V are constant ,

$P_1 \ V_1 = P_2 \ V_2$

$$\text{or } \frac{2}{3} \times \frac{1}{2} m_1^2 n_1^2 c_1^2 = \frac{2}{3} \times \frac{1}{2} m_2^2 n_2^2 c_2^2$$

But it is known that, at constant temperature, the mean kinetic energy of each molecule to two gases is equal irrespective of their size.

$$\text{so } \frac{1}{2}m_1^2c_1^2 = \frac{1}{2}m_2^2c_2^2$$

Therefore from the above two equations ,

$$n_1 \quad = \quad n_2$$

Hence the Avogadro's law.

Derivation of Graham's law diffusion from kinetic gas equation.

According to kinetic theory of gases,

$$PV = \frac{1}{3}mnc^2$$

$$\therefore mnc^2 = 3PV$$

$$c = \frac{3PV}{mn}$$

$$\text{or } c = \sqrt{\frac{3PV}{mn}}$$

$$\text{But} \quad \frac{m}{V} = \text{density}$$

$$c = \sqrt{\frac{3P}{\rho}} \quad \text{where } \rho \text{ is the density}$$

That is the root mean square velocity of a gas is $\alpha 1/\rho$ which is directionaly α to diffusion and hence the Graham's law of diffusion.

KINETIC ENERGY AND TEMPERATURE: or

Kinetic theory and temperature. or

Boltzman constant:

Let us say that, one mole of gas is taken for our study about temperature and kinetic energy.

The equation of kinetic theory for one mole of gases will be,

$$PV = \frac{1}{3}mNc^2 \qquad (\text{ N = Avogadro number})$$

Rewriting the above equation we may have,

$$PV = \frac{2}{3}\times\frac{1}{3}mNc^2$$

$$PV = \frac{2}{3}E_t \quad \text{--------------------------} \quad 1$$

Where K_t is the translational kinetic energy of one molecule of the gas.

But the ideal gas equation, for one mole of gas will be,

$$PV = RT \quad \text{------------------} \quad 2$$

From equation -1 and -2, we get,

$$\frac{2}{3}E_t = RT$$

$$\text{or } E_t = \frac{3}{2}RT \quad \text{-----------------} \quad 3$$

From equation -3 it is clear that, the translational kinetic energy, k_t of a molecule is

independent of volume,

independent of pressure,

independent of molar mass,

independent of nature of the molecules

but depends only on the absolute temperature . Thus , a molecule of Hydrogen gas has the same translational energy as that of any ideal gas molecule. But molecular velocities will be different for each gas.

The average translational kinetic energy of one molecule of and ideal gas is,

$$E_t = \frac{KE}{N} = \frac{RT}{N} = \frac{3}{2}KT$$

Where K (=R/N), is the Boltzmann constant. Thus it is clear that, Kinetic energy of an ideal gas is absolute temperature.

MAXWELL’S distribution of molecular velocities.

It is known that, all molecules can not be moving with the same speed. Moreover because of the inter molecular collisions, their speeds are changing billions of times every second. It is therefore impossible to know the speed of an individual molecule in a sample, since one mole contains 6 . 022 X 10 molecules.

Therefore it will be possible and useful to calculate the number of molecules which have a range of speed.

To do this let us consider a gaseous molecule with mass ‘m’ , having the velocity component ‘u’.

Therefore the kinetic energy associated with this velocities,

$$KE = \frac{1}{2}mu^2$$

The probability that this molecule has a velocity component ‘u; and ‘u + du’ is given by the function f(u).du

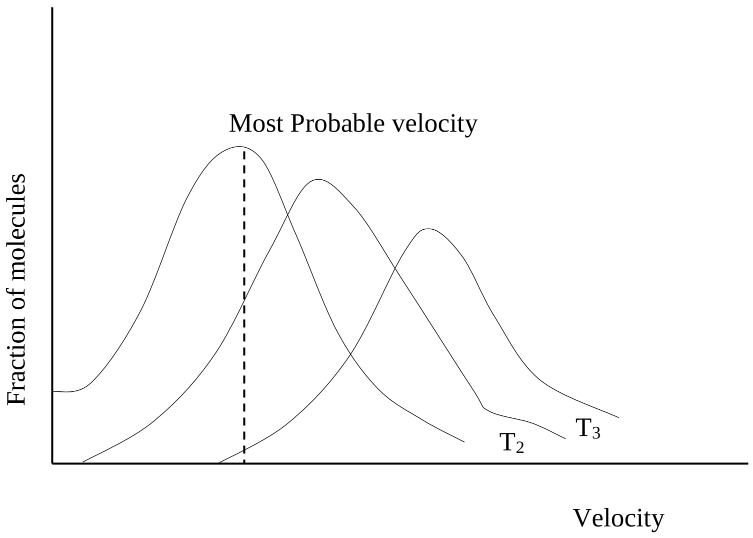
Maxwell and Boltzmann derived from statistical considerations, an expression for the distribution of molecules, between different possible velocities as given below.

$$f(u).du = = \frac{dN_u}{N} = 4\pi\left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}} \times e^{-Mc^2/2RT}.u^2.du$$

This equation is the mathematical form of Maxwell’s law of distribution of molecular velocities,

Where $\frac{dN_u}{N}$ is the fraction of molecules with velocities between u and u+du.

The Maxwell’s distribution of molecular velocities is plotted in the following plot.



Maxwell's distribution of velocities.

$e^{-Mc^2/2RT}$ is called the Boltzmann factor.

Special features.

From the Maxwell's velocities distribution curves we can have the following observations.

1. The area below the curve represents the total number of molecules, where as a point on the curve represents only the fraction of the molecules.
2. From the curve, it is clear that, the fraction of molecules having velocity, greater than zero, increases with increase in velocity, reaches a maximum and then falls off again towards zero at higher velocities.
3. The fraction of molecules with very low or very high velocity is very small.
4. There is certain velocities for which, the fraction of molecules is the maximum. This velocity is called the most probable velocity.

Effect of temperature on distribution of molecular velocities.

1. The most probable velocity increases with increase in temperature.
2. The rise in temperature increases the fraction of molecules having high velocities.
3. As the temperature rises, the peak moves to the right, showing that the velocity increases.
4. The peak becomes more flat at high temperature, than at low temperature, showing the increase in number of molecules with higher velocity.

Types of molecular velocities.

Three types of velocities are known as mentioned below.

1. The most probable velocity c
2. The average velocity c
3. The root mean square velocity c

Most probable velocity.

"The velocity possessed by the maximum number of molecules at a given temperature is called the most probable velocity.

Mathematically $c_{MP} = \sqrt{\frac{2RT}{M}}$

The average velocity.

The average of the speed possessed by various molecules is called the average velocity. Mathematically it can be represented as

$$c_{AV} = \left[\frac{8RT}{\pi M}\right]^{\frac{1}{2}}$$

Root mean square velocity.

The root mean square velocity of the molecules is given by,

$$c_{RMS} = \left[\frac{3RT}{M}\right]^{\frac{1}{2}}$$

Example.

Calculate the (i) MPV, (ii) AV and (iii)RMS of the Nitrogen molecule at 300k and 70 torr.

Solution.

$R = 8.314 Jk\ mol^{-1}$

$T = 300k$

$M = 2 \times 14 = 28g$ or $0.028\ kg\ mol^{-1}$

i) RMS $= \left[\frac{3RT}{M}\right]^{\frac{1}{2}}$

$$= \left[\frac{3\times80.314\times300}{0.028}\right]^{\frac{1}{2}}$$

$$= 516.95 \text{ m s}^{-1}$$

ii) AV = $\left[\frac{8RT}{M}\right]^{\frac{1}{2}}$

$$= \left[\frac{8\times0.314\times300}{3014\times0.028}\right]^{\frac{1}{2}} = 476.39 \text{ m s}^{-1}$$

iii) MP = $\left[\frac{2RT}{M}\right]^{\frac{1}{2}}$

$$= \left[\frac{2\times8.314\times300}{0.028}\right]^{\frac{1}{2}}$$

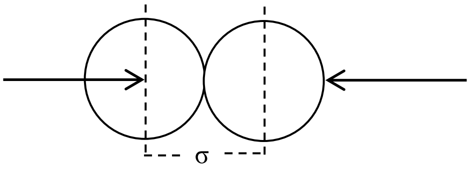
$$= 422.08 \text{ m s}^{-1}$$

COLLISION DIAMETER:

Kinetic theory of gases considers, the molecules as point mass. When two molecules approach each other, a point is reached at which, the repulsive forces become stronger, so that, the molecules have to retrace their path.

The distance between the centres of the two molecules at the point of their closest approach is called the collision diameter. It is represented by .

The collision diameter can be schematically represented as follows.



collision diameter

Therefore it is clear that, if the distance between the two centres of the molecules is less than - a collision ‘ which is an event in which the centres of two identical molecules come with in a distance of s - from each other ‘, takes place.

That is a moving molecule collide with another molecule, which lie with in the cylinder of radius .

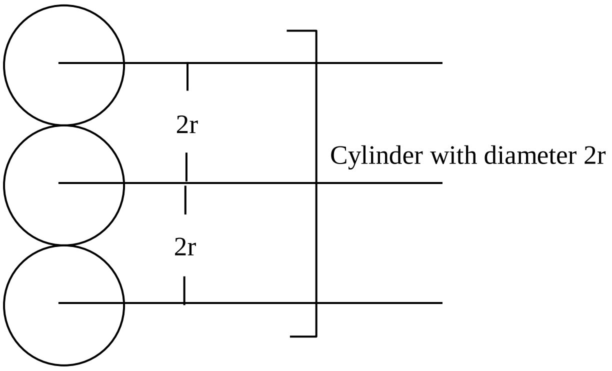
The volume $4/3Ps^3$ is called the effective volume of the molecule.

COLLISION FREQUENCY:

The number of collisions experienced by a molecule with another, per unit time per unit area is called the collision frequency. It is represented by ‘Z_{11} ‘.

To calculate the value of Z - let us say that molecule with radius ’r’ are moving in a vessel with volume ‘v’.

Let its average velocity is u_{AV} . When a molecule moves, it collides with other molecule which is lying with in a cylinder of radius 2r. This can be schematically represented as below.



The volume of the cylinder V_S - will be

$V_S = P (2r)^2 . h$ (h = height of the cylinder)

i.e $= P (2r)^2 . u$ (since h = u the distance travelled)

$V_S = Ps^2 . u$ (where 2r = the collision diameter)

If the number of molecule per unit volume is ‘n’,

then number of collisions for ‘n’ molecules is ,

$Z_1 = Ps^2 u n$

Here Z_1 - is the number collisions made by the given molecules with other molecules.

Therefore the number of collisions for all molecules in unit volume per second is

$Z_{11} = Ps^2 u . n . n$

$= Ps^2 u. n$

In a mixture of two gases, the relative velocity will be 2 u.

The collision frequency in a mixture of two gases is,

$A_{1,2} = 2 u Ps^2 u n^2$

Since each collision involve two molecules, the collision frequency for a single molecule,

$$\frac{Z_{1,2}}{2} = \frac{\sqrt{2}\Pi\sigma^2 un^2}{2}$$

$$Z = \frac{1}{\sqrt{2}}\Pi\sigma^2 un^2$$

Since u = $= \frac{\sqrt{8RT}}{\Pi M}$

$$Z = \frac{1}{\sqrt{2}}\Pi\sigma^2 \frac{\sqrt{8RT}}{\Pi M}.n^2$$

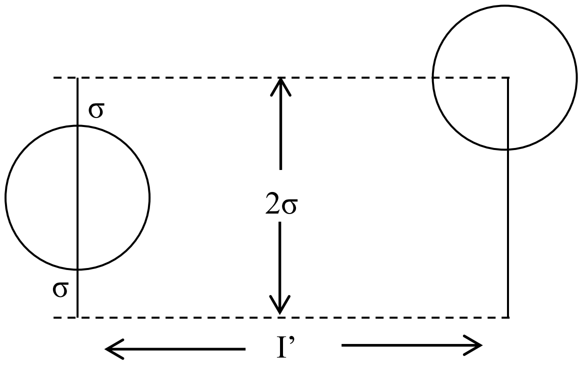
$$Z = \frac{1}{\sqrt{\cancel{2}}}\Pi\sigma^2 .2.\sqrt{\cancel{2}}\frac{\sqrt{RT}}{\Pi M}.n^2$$

$$Z = 2\sigma^2 n^2 \frac{\sqrt{RT}}{M}$$

MEAN FREE PATH:

The average distance that a molecule travels, before it comes in collision with another molecule, is called the mean free path.

Imagine a molecule moving in a given space, while all the molecules are at rest and let l'- be the mean free path, under these conditions and ' ' , the collision diameter as shown in the figure.



It is clear from the above figure that, on an average, each molecule occupies a cylindrical space of radius and length l'.

The volume occupied by each molecule $= \pi\sigma^2 \rightarrow (1)$

If 'v' cc of a gas contains 'N' molecules, then volume occupied by each molecule,

$$= \frac{V}{N} \rightarrow (2)$$

From -1 and -2 we have,

$$\Pi\sigma^2 l' = \frac{V}{N}$$

$$\therefore l' = \frac{V}{\Pi N\sigma^2}$$

But when all the molecules are in motion, the average mean free path,

$$l = \frac{l'}{\sqrt{2}}$$

$$\therefore l = \frac{V}{\sqrt{2}\Pi N\sigma^2}$$

If 'n' is the number of molecules in 1 cc of the gas then,

$$l = \frac{1}{\sqrt{2}\Pi N\sigma^2} \qquad \text{............(3)}$$

But we know that PV = n RT.

For one mole $PV = \frac{nRT}{N}$

or PV = nKT (since R/N = K)

From the equation PV = nRT we get n = P/RT (for 1 cc of the gas)

Substituting the value of ‘n’ in the equation -3 we get,

$$l = \frac{KT}{\sqrt{2}\Pi N\sigma^2}$$

Degrees of freedom of gaseous molecules.

Degrees of freedom of a molecule may be defines as the independent number of parameters, which must be specified to describe the state of or position of the molecule completely.

Since each atom of a molecule has 3 - degrees of freedom, a diatomic molecule will have six, a tri atomic molecule will have a nine and a poly atomic molecule will have in general 3N - degrees of freedom, where ‘N’ is the number on atoms in the molecule.

These degrees of freedom can be classified as follows.

1. Translational freedom,

2. Rotational degrees of freedom and

3. Vibrational freedom, depending on the modes translation, rotation and vibration possessed by the molecules.

Translational degree freedom.

To locate the position, that is the centre of mass of mono or poly atomic molecule in space, three independent parameters namely coordinates, y, and z are needed. Thus all molecules have three degrees of translational freedom.

If ‘u’ is the speed of a molecule, then its components in three coordinates will be u_x, uy and u_z.

$$u = u_x + u_y + u_z$$

A moving molecule will have a kinetic energy,

KE = 1/ mu

i.e. $KE = 1/2\ mu_x + 1/2mu_y + 1/2\ mu_z$

i.e $KE = KE_x + KE_y + KE_z$

Thus it is clear that, like the speed, kinetic energy can also be resolved in to three components along the three coordinate axes.

Rotational degree of freedom.

The rotational energy of a body is the energy possessed by its rotation about an axis passing through its centre of gravity.

A mono atomic molecule can rotate as a ball rolling on the ground and so has only one degree of freedom.

A diatomic or a poly atomic linear molecule behaves as a rigid rotor and therefore not free to rotate about the axis passing through the nuclei of the bonded atoms. Therefore it has only two rotational degree of freedom.

A non linear tri or poly atomic molecule have three rotational degree of freedom along the three mutually perpendicular axes.

$E_{rot} = 1/2 \qquad + 1/2 \qquad + 1/2$

Where $\square_x$, $\square_y$ and $\square_z$- are the angular velocities along the x, y and z axes and □ - is the moment of inertia.

Thus the it is seen that the rotational energy can also be resolved in to three components along the three coordinate axes.

Vibrational degree of freedom.

Bonds in a molecule may be regarded as frictionless and weightless springs of definite strength. Therefore the atoms in a molecule can make simple harmonic motions about their mean positions. During the motions, the bonds will compress and stretch alternately.

Let us consider a molecule containing ‘N’ atoms. Each one of the atom independently have three degrees of freedom, about three axes.

Therefore the total number of degree of freedom of the molecule with N - atom will be = 3N.

Out of these, the molecule will have 2 - rotational degree of freedom if linear and 3 - rotational degree of freedom if non linear.

Therefore the vibrational degree of freedom,

for a linear molecule will be = 3N - 3 - 2 = 3N - 5

for a non linear molecule = 3N - 3 - 3 = 3N - 6

For example a linear diatomic molecule will have,

3 X 2 - 5 = 6-5 = 1 degree of freedom.

For a triatomic molecule,

$3 \times 3 - 5 = 9 - 5 = 4.$

That is,

one symmetric stretching,

one asymmetric stretching and

two bending mode of vibration.

The vibrational energy is the combination of KE and PE

$E_{vib} = 1/2\ \square\ v^2 + 1/2K(r - r_o)$

Where □ is the reduced mass

v is the velocity of vibration and

r_o is the equilibrium position of the coordinates.

Thus the vibrational energy is also resolved in to various vibrational modes. depending on the molecule.

Principle of equipartition energy.

We know that the relative velocity of a moving particle is given by,

$U^2 = u_x{}^2 + u_y{}^2 + u_z{}^2$

Multiplying on both sides by 1/2m, we get,

$$\frac{1}{2}mu^2 = \frac{1}{2}mu_x^2 + \frac{1}{2}mu_y^2 + \frac{1}{2}mu_z^2$$
$$\text{i.e. } KE = KE_x + KE_y + KE_z$$

Since the molecule move in a random manner in the container, they don’t have any preferential directions.

$u_x = u_y = u_z$

Therefore we have

$$\frac{1}{2}mu_x^2 = \frac{1}{2}mu_y^2 = \frac{1}{2}mu_z^2$$
$$\text{i.e. } KE_x = KE_y = KE_z$$

From kinetic theory of gases we know that KE = 3/2 KT

$KE_x = KE_y = KE_z = 1/2\ KT$

Thus it is clear that, the energy term of all components contribute equally to the total energy.

This is called the principle of equipartition of energy and according to the principle " if a gaseous species has n - translational degrees of freedom, n_2 - rotational degrees of freedom and n_3 - vibrational degrees of freedom, then the

$$\text{total energy is} = n_1 \frac{KT}{2} + n_2 \frac{KT}{2} + n_3 \frac{KT}{2}$$

5.1.2 BEHAVIOUR OF REAL GASES:

An ideal or a perfect gas is one which obeys the gas laws or the gas equation PV = nRT strictly for all values of temperature and pressure.

But in actual practice, the gases obeyed the gas laws, more and more, as the temperature of gas raised more and more above their boiling points.

That is the gases obeyed gas laws at low pressure and at high temperature and disobeyed completely at high pressure and at low temperature.

This property of gases is called the deviation from ideal behaviour.

Compressibility factor.

The deviation of any gas from ideal behaviour can be best represented in terms of compressibility factor 'Z' which is defined as

$$Z = \frac{PV}{(PV)_{ideal}} = \frac{PV}{nRT} \quad (\sin ce\,(PV)_{ideal} = nRT)$$

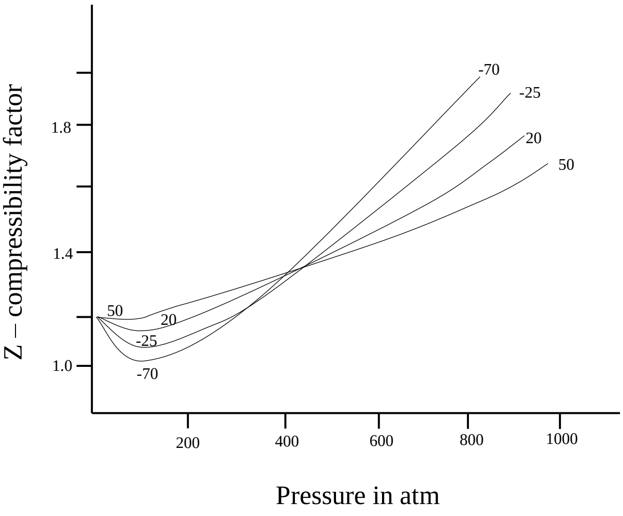
For an ideal gas Z = 1, under all conditions of temperature and pressure. The deviation of z - from unity thus gives the measure of imperfection of gas under consideration.

DEVIATION FROM BOYLE' S LAW: or

Boyle temperature. or

Effect of temperature on deviation.

The effect of temperature on deviation from ideal behaviour can be explained from the Z - P plots which are as shown below.



It is seen from the plot, that as the temperature is raised, the dip in the curve becomes smaller and smaller. At 323k, the curve is almost horizontal for an appreciable range of pressure between 0 - 100 atmosphere, which shows Z = almost ‘1’.

In other wards, PV is constant and hence Boyle’s law is obeyed at 323k for the range pressure 0 - 100 atmosphere.

The temperature namely 323k at which the gas obeys boyle’s law, for given range of pressure namely 0 - 100 atmosphere is called the Boyle temperature or Boyle point.

Below this Boyle temperature Z - decreases at first, approaches a minimum and increases continuously as the pressure is increased.

The Boyle temperature is different for different gases.

Explanation of deviation.

In order to explain the deviation from ideal behaviour of gases, some modification was needed for kinetic theory of gases. The following two postulates of ideal gas were found responsible for the deviation.

Postulate -1 the negligible volume.

The kinetic theory of gases assumed that the volume occupied by the gas molecules themselves are negligible one as compared to the total volume of the gas.

This postulate can be justified under ordinary conditions of temperature and pressure. But if the pressure is too high say 100 atmosphere or more, then the total volume of the gas will decrease appreciably so that, the volume of the molecules is the same as total volume of the gases. Under this condition, the volume occupied by the gas molecules will be no longer negligible as compared to the total volume.

In a similar way, if the temperature of the gas is lowered to a large extent, the total volume of the molecules decreases considerably, so that the volume occupied the molecules become appreciable.

Therefore the postulate -1 is not valid at high pressure and at low temperature.

Postulate - 2 inter molecular forces of attraction.

The theory assumes that, the inter molecular forces attraction between molecules are negligible. This assumption may be valid at low pressure and at high temperature, when the molecules will be far apart from one another.

But at high pressure or at low temperature, the volume will be small therefore the molecules be closer to one another. At this condition, inter molecular forces of attraction can't be ignored.

Hence this postulate also doesn't hold good at high pressure and at low temperature.

Thus it becomes necessary to apply suitable corrections to ideal gas equation so that it can be applied to real gases.

VIRIAL - equation. (virial means force) or

Kammerlingh - Onnes Virial equation.

In an attempt to derive a useful equation of state, that can be applied at all conditions of pressure and temperature, Kammerlingh and Onnes developed an equation called the Virial equation.

Kammerling and Onnes equated the PV/RT - term to a unity plus a series of correction terms as follows.

$$PV = RT\left(1 + \frac{B}{V^2} + \frac{C}{V^2} + \frac{D}{V^2} + ...\right) \rightarrow (1)$$

In terms of pressure the virial equation was represented as,

$$PV = RT\ \left(1 + B(T)P + C(T)P^2 + D(T)P^3 + ...\right) \rightarrow (2)$$

The equation expresses, PV - as a power series of pressure. At any given temperature, B, C, D etc. are called the Virial coefficients and these are functions of temperature.

At low temperature, all other terms cancel out and therefore PV=RT.

But as the pressure increases the pressure term becomes significant.

B term is the second, C is the third and so on virial coefficients which are considered to represent the effects of collision between two or three molecules respectively.

Derivation of the principle of corresponding states.

van der Walls showed that, if the pressure, volume and temperature are expressed in terms of critical state, we can obtain an important generalisation called 'the principle of corresponding state'.

The van der Wall's equation, for one mole of a gas is

$$\left(P+\frac{a}{v_m^2}\right)\left(v_m-b\right)=RT \quad \rightarrow (1)$$

Now let $P/P_C = P_r$; $V/V_C = V_r$; and $T/T_C = T_r$

where the subscripts 'c' represents the critical state and 'r' represent the reduced state respectively.

$P = P_rP_C$; $Vm = V_{m,c}\, V_r$ and $T = T_rT_C$

Substituting these values in the equation - 1

we get, $$\left(P_rP_c+\frac{a}{V_r^2V_{m,c}^2}\right)\left(V_rV_{m,c}-b\right)=RT_rT_c \quad \rightarrow (2)$$

Since $V_C = 3b$

$P_C = a/27b^2$

and $T_C = 8a/27Rb$

we can substitute these values in equation in - 2 and thus -2 becomes,

$$\left(\frac{aP}{27b^2}+\frac{a}{9V_r^2b}\right)\left(3V_rb-b\right)=RT_c\left(\frac{8a}{27Rb}\right) \quad \rightarrow (3)$$

After multiplying all terms by 27, we get ,

$$\text{or}\left(Pr+\frac{3}{V_r^2}\right)\left(3V_r-1\right)=8T_r \quad \rightarrow (4)$$

Equation - 4 doesn’t involve R or van der Wall’s constants ‘a’ and ‘b’. Therefore - 4 becomes a general equation, which can be applied to all substances.

It is clear from the equation, that two or more substances having the same reduced temperature and pressure, will have the same reduced volume.

This state is known as the principle of corresponding states.

Thus two or more substances, having the same reduced temperature and reduced pressure and therefore having the same reduced volume, are said to be in corresponding sates,

5.2 .1 THE LIQUID STATE:

Introduction.

Different kinds of matter, whether solid, liquid or gas consist of molecules which attract each other.

In solids, the molecules are very close to each other so that, the forces of attraction are sufficiently strong to hold them in a definite pattern. Therefore the solids maintain a definite shape and volume.

But the molecules in the liquids are comparatively farther apart and therefore, the forces of attraction are much smaller when compared to that in solids. Therefore although liquids have definite volume, they doesn’t maintain definite shape and take the shape of the vessel in which they are placed.

On the other hand in gases, the molecules are comparatively very far apart, so that the forces of attraction are negligibly small. Therefore the molecules are free to move in any direction in space and hence they have neither volume nor shape of their own. As a result, the gases assume the shape and volume of its container.

5.2.1 STRUCTURE OF LIQUIDS :

The liquid state may be considered as an intermediate state between the gaseous and the solid state of matter, because liquids can be obtained by cooling the gases under pressure or by the melting solids.

But a liquid is regarded as an extremely non ideal gas. In other words, it is a gaseous state in which there are short range of inter molecular forces of attraction. This is a reasonable explanation because, close to the critical points, there is no distinction between the liquids and gases.

EVAPORATION :

All we know that, a liquid placed in a open vessel, disappears gradually. For example, we can see liquid Bromine changing to reddish brown vapors and disappearing finally.

Thus the process of change of liquid in to vapor is called evaporation.

MECHANISM OF EVAPORATION :

We know that, the molecules of liquids are held together by attractive forces and are in constant motion. So the moving molecule will have kinetic energy and the average kinetic energy of a molecule will be constant at constant temperature. But we know that all the molecules are not having the same kinetic energy. The kinetic energy of molecules will range from very low to very high value. More over, there is exchange of kinetic energy during collisions experienced during their motion. As a result, the highly energetic fraction of molecules at the surface, overcome the inter molecular forces of attraction and escape as vapor. Thus little by little, all liquid molecules escape in to vapor phase.

It was found that evaporation is accompanied by cooling. This is because, as the more energy molecules go in to vapor, only the less energetic molecules remain in liquid. This results in the decrease in the temperature.

Since the temperature remains constant the average kinetic energy of remaining molecules also must be constant and therefore the evaporation continues till the lost molecule in the liquid state.

Factors affecting evaporation :

1. Nature of the liquid .

The ability of a liquid molecule to evaporate depends upon the strength of its intermolecular forces of attraction. It was found that, the more the intermolecular forces of attraction, the less is its ability to evaporate.

For example, ethers evaporate more readily than alcohols which in turn evaporate more readily than water. This is because the inter molecular forces of attractions these liquids in the following increasing order.

Ether < Alcohol < Water.

2. Surface area.

It is known that, the process of evaporation is a surface phenomenon. Therefore, the larger the surface area, the more must be the evaporation. It is because, more surface area give more opportunity to greater number of molecules to escape.

Thus the rate of evaporation of a given liquid is directly proportional to its surface area.

3. Temperature.

The increase in temperature increases the average kinetic energy of the liquid molecules. This makes larger number of molecules to attain sufficient energy for evaporation. Therefore, the rate of evaporation increases with increase in the absolute temperature.

4. Flow of air current over the surface.

The molecules passed in to vapor phase may again be liquefied and pass in to liquid state. But an air flow over the surface of the liquid, takes away the evaporated molecules, which prevents them again going in to liquid state. More over, a vacuum is produced temporarily on the surface, which allows more molecules to evaporate.

Thus the flow of air current over the surface, increases the rate of evaporation.

VAPOR PRESSURE :

Liquids placed in an open vessel goes on evaporating, till the last liquid molecule present, and finally vanishes.

But on the other hand, liquids placed in a closed vessel, doesn’t continue evaporating indefinitely. This fact can be explained as follows.

The evaporation of the liquid, goes on by increasing the number of free molecules over the liquid surface. During the random motion of the vapor molecules, more of them strike the liquid surface and are captured bey liquid molecules. This process is called condensation.

This process of condensation and evaporation proceed simultaneously. In this reversible process, a condition is reached, where the rate of condensation becomes equal to the rate of evaporation. Such a state in which the condensation and evaporation proceed with equal rate but in opposite direction is called ‘ the state of dynamic equilibrium ‘.

At this state obviously, there will be no change in the relative concentrations of the vapor and the liquid state.

Now at a given temperature, the pressure of the vapor in equilibrium with the liquid will be a constant .

Thus’ the pressure of the vapor in equilibrium with its liquid at a given temperature is called the equilibrium vapor pressure or simply the vapor pressure’.

Since the pressure of a gas is given the gas equation

$$PV = nRT$$

$$P = RT\frac{n}{V}$$

$$= CRT$$ (where 'C' is the concentration of vapor in moles dm)

VAPOR PRESSURE AND BOILING POINT:

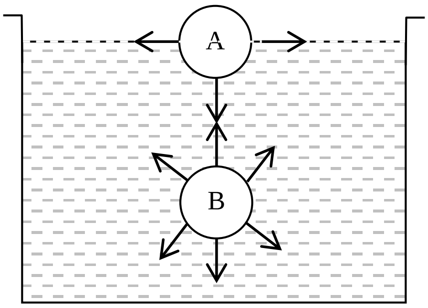
The area above the liquid kept in an open vessel experiences the atmospheric pressure, which suppresses the escape of liquid molecules in to vapor phase. But if we rise the temperature of the liquid, more and more of the liquid molecules escape in to vapor phase, by increasing the vapor pressure over the liquid surface. This increase in vapor pressure opposes the atmospheric pressure and a state is attained, when the vapor pressure exceeds the atmospheric pressure. At this state liquid molecules escape in to vapor phase freely, by making bubbles.

This 'temperature at which the liquid molecules escape freely in to vapor state is called its boiling point'.

Or in other words 'the boiling point of a liquid is defined as the temperature at which the vapor pressure of the liquid becomes equal to the atmospheric pressure'.

SURFACE TENSION :

Consider two molecules A and B of a liquid and say that A is in the middle and B is at the surface of the liquid as shown below.



Molecule B is lying in the middle and therefore it will be pulled by the neighbouring molecules equally in all directions. Hence the resultant force on B will become zero.

As for as A is concerned which is lying at the surface, there is no molecule above it. But by its side only limited number of molecules, where as there are so many molecules below it. As a result, the molecule A experiences a resultant down ward pull. This is the case with all the molecules lying at the surface of the liquid.

Due to this resultant down ward pull, all the surface molecules tend to leave the surface and therefore, the surface behaves like a stretched membrane under tension.

This force acts down wards perpendicular to the surface and pulls the molecules at the surface down wards. This force per unit area is called surface tension.

Thus surface tension is defined as ‘the force in dynes acting at right angles to the surface of liquid along 1 - cm length of the surface’.

It is represented by ‘ ‘.

Mathematically it can be represented as,

$$\gamma = \frac{\text{work done}}{\text{change in area}} \text{Nm}^{-1}$$

Due to surface tension, a liquid tends to minimise its surface area. For a given volume of a liquid, sphere has the minimum surface are. That is why small drops of liquids are spherical.

TROUTON’S RULE:

The Trouton’s rule says that, the molar heat of vaporisatiion of a liquid in Joules divided by its normal boiling point on absolute temperature is approximately equal to ‘88’.

Mathematically Trouton’s rule can be represented as ,

$$\frac{\Delta H_v}{T_b} \approx 88 J^{-1} mol^{-1}$$

Where ΔH_v is the molar heat of vaporisation and is the normal boiling point.

The value $\frac{\Delta H_v}{T_b}$ is called the entropy of vaporisation.

Example .

Assuming that it obeys Trouton’s rule, calculate the molar heat of vaporisatiion of n - Heptane whose boiling point is 309k.

Solution.

$T_b = 309k$

We know that $\frac{\Delta H_v}{T_b} \approx$

i.e. $\frac{\Delta H_v}{309} \approx 88$

$$\Delta H_v = 88 \times 309 = 27192 Jmol^{-1}$$

SURFACE ENERGY :

It is clear that the effect of surface tension is to reduce the area of the surface to a minimum. Therefore in order to over come this effect, that is to increase the area of the surface of a liquid, we have to work against the force of surface tension.

Thus the work required to be done, in order to extend the area of the surface of a liquid by one cm is called the surface energy.

The surface energy is expressed in ergs cm and can also be put in dynes cm .

Interfacial tension.

The force acting per unit length along the interface between two liquids is called the interfacial tension.

The interfacial tension is less than the surface tension of the liquids with higher value.

Some effects on surface tension.

1. Effect of temperature on surface tension.

It is observed that, the surface tension of liquids, decrease with increase in temperature.

It is because, the van der Walls forces of attraction decreases withe increase in temperature.

The relation between surface tension and the absolute temperature is given by Ramsay - Shield equation as given below.

$$\gamma\left(\frac{M}{\rho}\right)^{\frac{2}{3}} = K\left(T_c - T - 6\right)$$

Where M = Molar mass of the liquid
= is its density
= the critical temperature
T = the absolute temperature and
K = is a constant.

2. Effects of solute on surface tension.

The surface tension of a liquid varies, when a solute is added to it. The variation depends on the nature of the solute as detailed below.

a). If the solute is a liquid and its surface tension is nearly equal to that of the solvent, then the surface tension of the resultant mixture varies linearly with the mole fraction of the solute.

b). If the solute is a liquid and its surface tension is much smaller when compared to that of the solvent, then the surface tension of the resultant mixture decreases to a large extent with the mole fraction of the solute.

It is because, the solute molecules with low surface tension, accumulate at the surface, which decreases the surface tension of the resultant mixture.

For example, substances like soap and detergents behave in this manner and these compounds are called the surface acting substances.

Surface tension applied to every day life.

In day to day life, we are using soap and chemical detergents for cleansing purposes. The mechanism of cleansing can be explained as follows. Water has higher surface tension where as soap solutions has lower surface tension. During cleansing, the soap solution with lower surface tension, penetrates in to the fibre and surround the greasy substances. As a result of it, the interfacial tension between water and the greasy material is reduced. Therefore the greasy materials are easily removed from the material.

VISCOSITY:

The property of the liquids which determine their rate of flow from higher level to lower level is called the viscosity of the liquids.

e.g.

substances like Glycerine and molasses flow very slowly and these substances are said to have high viscosity.

Liquids like Water and ether flow at a faster rate and such liquids are said to have low viscosity.

Thus the rate of flow of liquids is 1/ viscosity.

Explanation.

A liquid flowing through a tube may be assumed as made up of series of concentric cylinders.

The cylindrical layer of the liquid which wets the tube is in contact with the walls of the tube and must be stationary. The adjacent layer slides with certain speed during the flow. In a similar way, the successive cylindrical layers slide with increasing velocity than the out side layer. The centre most layer will have the maximum velocity and the outer most layer will have the least velocity.

This relative motion of the adjacent layers of the liquid is opposed by an internal friction, which resists the sliding of the cylinders.

This internal resistance or the internal friction is called the viscosity of that liquid.

Coefficient of Viscosity.

'The force that must be exerted between two parallel layers of unit area and unit distance apart, in order to maintain a unit velocity of streaming of one layer past the other' is called the coefficient of viscosity or simply the viscosity '.

It is represented by ' ' and mathematically viscosity coefficient is,

$$\eta = \frac{\pi r^2 t \rho}{8VI}$$

Where = coefficient of viscosity,

V = volume of the liquid,

l = length of the tube,

r = radius of the tube,

t = time in seconds and

p = the driving pressure.

The reciprocal of viscosity is termed fluidity Φ and is given by,

$$\Phi = \frac{1}{\eta}$$

Liquids with low viscosity are called mobile liquids and those withe high viscosity are called viscous liquids.

Effect of temperature on viscosity.

The viscosity of a liquid decreases rapidly with increase in temperature.

The coefficient of viscosity in general related to its absolute temperature as follows.

$$\eta \ \alpha \ e^{E/RT}$$

Where E = the activation energy for viscous flow of the given liquid.

$$\eta = A e^{E/RT}$$

$$\text{or } \text{In}\eta = \text{In}A + \frac{E}{RT}$$

Now let as say that η_1 and η_2 are the coefficients of viscosity at temperatures T_1 and T_2 .

$$\therefore \ \text{In}\frac{\eta_1}{\eta_2} = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\text{or } \log\frac{\eta_1}{\eta_2} = \frac{E}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

After knowing all the values in the above equation, we can calculate the value of E.

REFRACTIVE INDEX :

When a ray of light passes from one medium to another medium, its direction is bent at the interface. This phenomenon is called refraction.

The refractive index - is given by

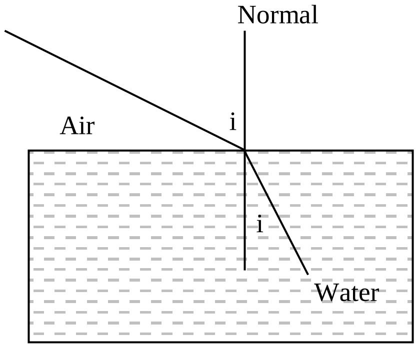
= sin’i’/sin’r’

Where = refractive index

i = angle of incidence and

r = angle of refraction.

If a ray of light passes from a lighter medium say air , in to a denser medium say water, then the light ray is refracted towards the normal, so that the angle of refraction ‘r’ is less than the angle of incidence ‘i’, as shown below.



The refractive index of a medium can also be defined as ‘the velocity of light in vacuum to that in the medium’.

Specific refraction.

Specific refraction is given the relation,

$$R = \left[\frac{\mu^2 - 1}{\mu^2 + 2}\right]\frac{1}{d}$$

Where R = a constant called specific refraction of refractivity

= refractive index and

d = the density of the liquid.

Molar refraction.

The product obtained by multiplying the specific refraction with the molar mass M_m - of a liquid is called the molar refraction.

$$R' = \frac{M_m}{d}\left[\frac{\mu^2 - 1}{\mu^2 + 2}\right]$$

Where R’ is the molar refraction or molecular refraction.

PHYSICAL PROPERTIES AND CHEMICAL CONSTITUTION:

Introduction.

The physical properties of liquids, such as molar volume, parachor refractive index etc. are divided in to two types namely,

1. Additive property and

2. Constitutive property.

1. Additive property.

That property of molecule, which is the sum of the corresponding properties of the atoms constituting the molecule is called the additive property.

e.g.

The molecular mass of a molecule is a very good example for additive property, because the molecular mass of any molecule is calculated by adding the atomic masses of the constituent atoms.

The molecular mass of Benzene with the molecular formula C_6H_6 is given as,

6C = 6X12 = 72

6H = 6X1 = 6

Total = 78.

2. Constitutive property.

That property of a molecule, which depends on the constitution of molecules or in other wards, the arrangement of atoms in the molecule is called the constitutive property.

e.g.

Optical activity.

Most of the physical properties of the liquids are partly additive and partly constitutive. Their study therefore proved useful in deciding the constitution of liquids in doubtful cases as detailed below.

MOLAR VOLUME AND CHEMICAL CONSTITUTION:

Molar volume of a substance is defined as the volume occupied by one mole of the substance.

That is molar volume $V_m = \frac{\text{moleculae mass}}{\text{Density}}$

Since molar volume is 22.4 liters for all cases at S.T.P, Kopp tried to find out, whether the uniformity existed in liquids also. Even though the uniformity of results which he was looking for was not available in his attempts, Kopp established the following facts.

That is “ the molar volume of a substance is approximately equal to the sum of the atomic volumes of its constituent atoms” which is known as Kopp’s law.

He also found that there was some regularities in the molar volumes of liquids as detailed below.

1. The isomers belonging to the same homologous series of organic compounds had nearly equal molar volumes.

For example,

the molar volume of n - Pentane was found to be = 162.8 ml

and the molar volume of iso Butane = 162.0 ml.

2. Any successive members of the same homologous series of organic compounds differed by the same amount of molar volume.

For example in aliphatic alcohols the difference is 21.4 ml,

in aliphatic acids the difference is 22.5 ml

This fact led Kopp to believe that, the molecular volume of a molecule is approximately equal to the sum of the atomic volumes of the elements constituting the molecule

From the experimental facts he calculated the atomic volumes of some atoms which can be tabulated as follows.

Element	Atomic volume
H	5.5
C	11.0
Cl	22.8
O in -OH	7.8
O in carbonyl	22.2
S	22.6

However it was found that, the molar volume of Oxygen in -OH group was different from that in carbonyl group. It was also found that, the presence of Benzene nucleus reduced the molar volume by 15.0 ml.

These facts led to the conclusion that, the molar volume is not purely an additive property but both additive and constitutional in nature.

Applications.

The molar volume of Acetone can be calculated as follows.

Molecular formula of acetone is CH_3COCH_3

The molar volume of 3C = 3 X 11.0 = 33.0

The molar volume of 6 H = 6 X 5.5 = 33.0

The molar volume of O = 1 X 12.2 = 12.2

Total = 78.2

The experimental value of molar volume can be calculated as follows.

Molecular weight of Acetone = 58

Its density at boiling point = 0.749

$$\text{The molar volume} = \frac{58}{0.749} = 77.4$$

Thus the experimental value closely agrees with the calculated value, showing that the composition Acetone is correct.

Draw back.

The property of molar volume has only limited scope in structural determinations.

PARACHOR AND CHEMICAL CONSTITUTION:

Macleod is 1923 showed that,

$$C = \frac{\gamma^{\frac{3}{4}}}{(D-d)} \rightarrow (1)$$

Where = surface tension,

D = the density of the liquid and

d = the density of the saturated vapor of the liquid at same temperature.

In 1924 Sugden obtained another equation by multiplying both sides of the above equation by Molecular weight M as given below.

$$MC = \frac{M\gamma^{\frac{3}{4}}}{(D-d)} = [P] \quad \rightarrow (2)$$

Sugden called this resulting constant [P] -as the parachor.

At ordinary temperatures, ‘d’ the density of the vapor is negligibly small as compared to ‘D’ and hence the equation -2 may be simplified as,

$$[P] = \frac{M\gamma^{\frac{3}{4}}}{D} \quad \rightarrow (3)$$

If the temperature is such that, =1, then the equation -3 simplifies to,

$[P] = \frac{M}{D} = V_m$ (where V_m is the molar volume)

Thus the parachor may be defined as ‘the molar volume of a substance when its surface tension is unity ‘.

Sugden on the basis of the following facts found that parachor is largely an additive property.

1. The isomeric compounds of the same family of organic compounds such as esters, alcohols etc. have almost the same parachor as tabulated below.

Ester	Parachor	Isomer	Parachor
Methyl valerate	292.5	iso amyl formate	293.6
Ethyl iso butyrate	292.5	iso butyl acetate	295.1
Ethyl butyrate	293.6	n - propyl propionate	295.3

2. The difference between the parachors of successive members of a homologous series is nearly constant as tabulated below.

Compound	M.F	[P]	Diff.in [P]	[P] of CH_2
Ethane	C_2H_6	110.5	40.3	40.3
Propane	C_3H_8	150.8		
Hexane	C_6H_{14}	270.1	119.3	39.8
Heptane	C_7H_{16}	309.3	39.2	39.2
Octane	C_8H_{18}	345.7	35.7	35.7

Decane	$C_{10}H_{22}$	424.2	79.2	39.6

The average value of a CH_2 - group corresponds to 39.0

ATOMIC PARACHOR :

It was found that, [P] - of Decane is 424.2 and the average value of parachor for group is 39.0

Since Decane molecule has 10 groups and two H - atoms,

10 + 2H = 424.2

But we know that the [P] - of a group is = 39.0

10 X 39.0 + 2H = 424.2

i.e. 390.0 + 2H = 424.2

or 2H = 424.2 - 390.0

or H = (424.2-390.0)/2

= 17.1

Thus the atomic parachor of H = 17.1

Now the parachor of CH_2 = 39.0

But we know that the atomic parachor of H - = 17.1

C + 2H = 39.0

or C + 2 X 17.1 = 39.0

i.e C + 34.2 = 39.0

2. The atomic parachor of C = 39.0 - 34.2 = 4.8

Thus by knowing the atomic parachors of C - and H - it is possible to calculate the [P] of all other atoms and the calculated value of ceratin atoms can be tabulated as follows.

Atom	[P]
C	4.8
H	17.1
N	12.5
O	20.0

Cl	54.3
Br	68.0
I	90.0
S	48.2
P	37.7

Structural parachor.

Parachor like molar volume, is largely additive but partly a constitutive property.

For example, on the basis of atomic parachor, the parachor of C_2H_4 must have the following value.

Parachor of C_2H_4 .

$2 X C = 2 X 4.8 = 9.6$

$4 X H = 4 X 17.1 = 68.4$

Total = 78.0

But the observed value is 99.5.

The difference is = 99.5 - 78.0 = 21.5

Hence it becomes clear that the double bond in ethylene must contribute the value of 21.5

Thus a careful examination of ethylenic double bonds showed that, a double bond has an average parachor contribution of 23.2. Similarly it was also found that a triple bond has an average contribution of 46.6.

Some of structural parachors can be tabulated as follows.

Structure	Parachor	Structure	Parachor
double bond	23.2	6 -membered ring	6.1
triple bond	46.6	Naphthalene ring	12. 2
dative bond	-1.6	O - in ester	60.0

Calculating the parachor of a compound.

For example, the [P] - of Acetone can be calculated by using the above table.

Molecular formula Acetone is C_3H_6O and it is having a an Oxygen atom in the ester bond.

The parachor of Acetone.

3 X C = 3 X 4.8 = 14.4

6 X H = 6 X 17.1 = 102.6

1- O = 1 X 20.0 = 20.0

1-double bond = 1 X 23.2 = 23.2

Total = 160.2

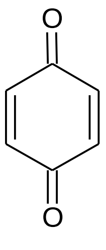
Therefore the calculated value of parachor for Acetone is 160.2, where as observed value is 161.1 which is good agreement.

Applications of parachor in deciding the constitution.

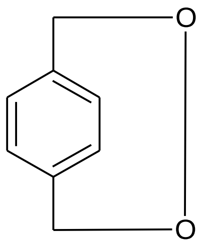
With the help of atomic and structural parachors, the parachor of a compound can be calculated. This value may be used to decide the correct structure of certain compounds which has alternate possibilities.

For example, the following two structures where assigned to Benzo quinone whose molecular formula si $C_6H_4O_2$.

$C_6H_4O_2$



(1)



(2)

The parachor for structure (1)

6C = 6 X 4.8 = 28.8

4H = 4 X 17.1 = 68.4

2 - O = 2 X 20.0 = 40.0 Total = 236.1

3 - double bond = 3 X 23.2 = 69.6

1, six membered ring = 1 X 6.1 = 6.1

Parachor of structure (2)

$$6\text{C} = 6 \times 28.8 = 28.8$$

$$4\text{H} = 4 \times 17.1 = 68.4$$

$$2\text{O} = 2 \times 20.0 = 40.0$$

$$3 - \text{double bound} = 3 \times 23.2 = 69.6$$

$$2, \text{six membered ring} = \underline{2 \times 6.1 = 12.2}$$

$$\text{Total} = \underline{\quad 219.0 \quad}$$

That is the calculated parachor value of - 1 is 236.1 and that of - 2 is 219.0. But the observes value of parachor for this compound is 236.8 which suggests structure (1) - for Quinoline.

Structure of iso - cyanide group.

Two structures possible for iso - cyanide group as shown below.

- N C	- N C
(1)	(2)

The parachor value for these two structures can be calculated as follows.

For (1)

$$1\text{N} = 1 \times 12.5 = 12.5$$

$$1\text{C} = 1 \times 4.8 = 4.8$$

$$1 - \text{double bond} = \underline{1 \times 23.2 = 23.2}$$

$$\text{Total} = \underline{\quad 40.5 \quad}$$

For (2)

$$1\text{N} = 1 \times 12.5 = 12.5$$

$$1\text{C} = 1 \times 4.8 = 4.8$$

$$1 - \text{triple bond} = 1 \times 46.6 = 46.6$$

$$1 - \text{dative bond} = 1 \times -1.6 = \underline{-1.6}$$

$$\text{Total} = \underline{\quad 62.3 \quad}$$

But the observed parachor value of cyanide group is 66.0. This value favours the structure (2) - for iso - cyanide group.

Parachor and association of molecules.

It is known that, certain compounds like water, Ethanol etc. undergo association, due to hydrogen bonding in the liquid state as shown below.

Et Et Et Et

O H O H O H O H

For such liquids, the calculated value of parachor is lower than the observed value.

Sidgwick explained that, the co - valency increase due to H - bonding is responsible for the parachor decrease.

That is due to the formation of H - bonding, a co - ordinate link is produced between O - and H - atoms and as a result the co - valency increase from 1 - to 2.

But it was found that, the parachor decrease for a dative bond is 1.6 and one co - valent bond is 12.8.

Therefore the total decrease for two molecules is

$$= -(12.8 + 1.6) = - 14 . 4$$

Therefore the decrease for one molecule = - 14.4 /2 = - 7.2.

The observed parachor of Ethanol at 293k is = 126.9

The calculated value of parachor is,

$$\begin{aligned} 2C &= 2\times 2.48 = 9.6 \\ 6H &= 6\times 17.1 = 102.6 \\ O &= 1\times 20.0 = \underline{20.0} \\ \text{Total} &= \underline{132.2} \end{aligned}$$

So after subtracting the decrease for association from the calculated value, we get the parachor as = 132.2 - 7.2 = 125.0

This resultant value obtained after the correction, agrees well with the calculated value.

But it was found that, the anomaly at lower temperature was high and at higher temperature it is low.

For example, the parachor values of Ethanol, at various temperatures is as given below.

Temperature	Parachor
243k	125.4
293k	126.9
473k	131.0

That is the calculated value namely 132.2 is in good agreement with the observed value 131.0 at 473k only. It is because at lower temperatures association is high and from the above values it is clear that at 243k Ethanol is completely in associated form only.

VISCOSITY:

Viscosity is neither an additive nor a constitutive property and therefore, it is not as useful as the other physical properties in deciding the chemical constitution.

But Dunstan discovered a relationship between viscosity and molecular volume for liquids, which are not associated, as given below.

$$\frac{d}{M}\times\eta\times10^{6}=40\text{ to }60$$

Where ‘d’ = the density of the liquid,

‘M’ = molecular weight of the liquid and

‘ ‘ = the viscosity.

It was found that, if the value exceeds ‘70’, it is an indication that, the molecule is an associated one. The value for certain compounds were found as given below.

Set - 1

Compound	The observed value.
Acetone	43
Toluene	57
Benzene	73

Set - 2

Compound	The observed value.
Water	560
Glycol	2750

Glycerol	116400

The set -1 molecules are in the non associated form and the set -2 molecules are in the associated form.

MOLAR REFRACTION:

The product obtained by multiplying the specific refraction of refractivity, with molar mass of a liquid is called the molar volume.

Mathematically it can be represented as,

$$R_m = \frac{M_m\left(\mu^2 - 1\right)}{d\left(\mu^2 + 2\right)}$$

Where R_m = molar refraction or Refractivity,

M_m = molar mass,

d = density and

= refractive index.

Since the angle of refraction depends on the kind, the number and the arrangement of atoms with in the molecule of the medium, this property can also be used in the determination of molecular structure.

Molar refraction was found to be an additive property. It was also found that , the difference in molar refraction of the successive members of a homologous series remained nearly constant as shown below.

e.g

Compound	R_m	Difference
Methanol	8.2	
Ethanol	12.8	= 4.6
Propanol	17.5	= 4.7
Butanol	22.1	= 4.6

Atomic and structural Refraction.

Atomic and structural refractions can be calculated as follows. For example the average value for a CH_2 - group is = 4.628 and the molar refraction of Hexane was found to be 29.09.

The molecular formula of Hexane is C_6H_{14}.

i.e. = 6 X +2 H

The molar refraction of 6 X + 2 H = 29.09

But the molar refraction of a group = 4.618

$$
\begin{aligned}
&\text{i.e} = 6 \times CH_2 + 2H \\
&\text{The molar refraction of } 6 \times CH_2 + 2H = 29.09 \\
&\text{But the molar refraction of a } CH_2 \text{ group} = 4.618 \\
&\therefore \quad 6 \times 4.618 + 2H = 29.09 \\
&\text{i.e} \quad 2H = 29.09 - 27.7 = 2.2
\end{aligned}
$$

The molar refraction of H- is $\frac{2.2}{2} = 1.1$

Now we know that the molar refraction of a OH_2 group is 4.618 and that of H - is 1.1.

$$
\begin{aligned}
&\text{i.e } CH_2 = 4.618 \\
&\text{or } C + 2H = 4.618 \\
&\text{or } C + 2 \times 1.1 = 4.618 \\
&\text{or } C = 4.618 - 2.2
\end{aligned}
$$

The molar refraction of C - is = 2.418.

Atomic and molar refractions of certain common elements and some structural refractions for Sodium D - line can be tabulated as follows.

Atom and structure.	Molar refraction.
C	2.42
H	1.1
O - in -OH	1.53
O - in -OR	1.64
O - in -CO	2.21
N - in - NH_2	2.32
Cl	5.97
Br	8.86
bond	1.73

bond	2.40

Using these constants, molar refractions of a substance can be calculated and by comparing it with the observe value, it is possible to confirm its constitution.

Example - 1.

For example the R_m - value of Benzene on the basis of its Kekule structure as given below can be calculated as follows.

Kekule structure of Benzene

$$
\begin{aligned}
6C &= 6\times 2.418 = 13.508 \\
6H &= 6\times 1.100 = 6.600 \\
3(=) &= 3\times 1.735 = \underline{5.199} \\
\text{Total} &= \underline{25.307}
\end{aligned}
$$

The observed R_m - value, 26.2 , which closely agrees with the calculated value and hence the Kekule structure assigned to Benzene is correct.

Example - 2, Keto - enol tautomerism.

The molecular formula of Ethyl aceto acetate or Aceto acetic ester is $C_6H_{10}O_3$ and the keto and enol structures are,

CH_3COCH_2COOEt	CH3 CH = CH COOEt
Keto form	Enol form

At ordinary temperatures the molar refraction of the Keto - form is,

$$
\begin{aligned}
6C &= 6\times 2.42 = \underline{14.52} \\
10H &= 10\times 1.1 = \underline{11.00} \\
2-O \text{ in } CO &= 2\times 2.21 = 4.42 \\
1-O \text{ in ester } &= 1\times 1.614 = 1.614 \\
\text{Total } &= 31.58
\end{aligned}
$$

Similarly the molar refraction for the enol - form is,

$$\begin{aligned}
6C &= 6\times 2.42 = 14.52 \\
10H &= 10\times 1.1 = 11.00 \\
1, O \text{ in } -OH &= 1\times 1.53 = \underline{1.53} \\
1, O \text{ in } OEt &= 1\times 1.64 = \underline{1.64} \\
1, O \text{ in } -Co &= 1\times 2.11 = 2.21 \\
1, (=) &= 1\times 1.73 = 1.73 \\
\text{Total} &= 32.63
\end{aligned}$$

Therefore the calculated of the keto form = 31.58

the calculated of the enol form = 32.63

the observed = 32.00.

Thus it is clear that the observed value is nearer to the calculated value for the keto form, showing that the, at ordinary temperatures, esters exist mainly in the keto - form only.

Example - 3, structure of Acetylene di bromide.

The structure assigned to Acetylene di bromide is as follows.

Br CH CH Br

Its molar refraction can be calculated as follows.

$$\begin{aligned}
2C &= 2\times 2.42 = 4.84 \\
2H &= 2\times 1.10 = 2.20 \\
2Br &= 2\times 8.86 = 17.72 \\
1, (=) &= 1\times 1.73 = \underline{1.73} \\
\text{Total} &= \underline{26.49}
\end{aligned}$$

The observed value 26.30 is in good agreement with the calculated value namely, 26.49 which in conformity with the structure assigned to the Acetylene di bromide.

Expected questions.

1. Calculate the energy of activation of Diethyl ether for viscous flow. Given that, the viscosity of Diethyl ether is 2.84 milli poise at 273k and 2.33 at 293k.
2. Calculate the R_m - value of Ethylene di chloride.
3. Explain the additive properties with examples.
4. Why liquids doesn’t have definite shape where as the solids have.
5. Define interfacial tension. Give its important in our day to day life.

NOTES

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

PRACTICAL - I

1. IN - ORGANIC QUALITATIVE ANALYSIS

SYSTEMATIN ANALYSIS OF GIVEN IN - ORGANIC MIXTURE CONTAINING TWO ACID RADICALS AND TWO BASIC RADICLS.

A. Prelimunary Tests.

Experiment	Observation	Inference
1. Colour and appearance The colour and the appearance of the mixture is noted	Blue or bluish green in colour.	Copper salts may be present.
	Green or pale green in colour	Copper Nickel or Ferrous salts may be present.
	Pink in colour	Cobalt or Manganese salts may be present.
	No characteristic colour	Copper, Cobalt, Nickel and Ferrous salts may absent.
2. Solubility test A small amount of the mixture taken in semi micro test tube shaken well with 2ml or water, centrifuge and divided in to two portions.		
To one portion 1ml of saturated solution of Sodium carbonate is added.	A white precipitate is formed	The mixture is partially soluble in water.
If no precipitate is formed, Nessler’s		Presence of Ammonium

reagent is added to another portion.	A reddish brown precipitate is formed.	salts.
	No reddish brown precipitate is formed	The mixture is insoluble in water.
3. Action of heat A small quantity of the mixture is taken in a dry test tube and heated strongly.	The mixture turns black	Copper salts may be present.
	Yellow when hot and white when cold	Zinc salts may be present.
	A white sublimate is formed along with liberation of ammonia gas	Ammonium salts may be present.
	A reddish brown gas rekindling a glowing splinter is produced	Presence of Nitrates.
	A colourless gas turning lime water milky is produced	Carbonates may be present
	No characteristic change is noted	Absence of copper, Zinc, Ammonium, Nitrate and Carbonate salts.
4. Flame test. A small amount of the mixture taken in a watch glass is mixed well with 2 or 3 drops of con.HCl and the paste is burnt is the blue Bunsen flame and the colour of the flame is noted	Burns with a blue or bluesh green flame	Presence of Copper salts
	Burns with a pale green colour	Presence of Barium of Borate salts.
	Burns with brick red colour	Presence of Calcium salts

	Burns with crimson red flame	Presence of Strontium salts
	No characteristic coloured flame is obesrved	Absence of Copper, Barium, Borate, Calcium and Strontium salts.
A small amount of the mixture is is taken along with a little of Calcium fluoride and made in to a paste with con. Sulphuric acid and then the past in burnt in the blue Bunsen flame withe the help of a glass rod	Burns with a dense green flame	Presence of Borate
	No characteristic coloured flame is noted	Absence of Borate.
A small amount of the mixture taken in a watch glass is made in to a paste with a pinch of Borax and con. Sulphuric acid and the paste is burnt is the blue Bunsen flame with the help of a glass rod..	Burns with a dense green colour	Presence of Fluoride salts
	Doesnot burn with dense green colour	Absence of Fluoride.

B. Preliminary tests for acid radical.

1. Test with dil. HCl		
A small amount of the substance taken in a test tube is treated with dil.HCl.	A colourless gas which turns lime water milky, is obtained with brisk effervescence in the cold.	Presence of Carbonate.
	No effervescence	Absence of carbonat
About 2ml of dil. Sulphuric acid is heated with a pinch of MnO$_2$ strongly, cooled and then a small amount of the mixture is added to it.	A colourless gas which turns lime water milky is obtained with effervescence.	Presence of Oxalate.
	No characteristic change	Absence of Oxalate
A small amount of the substance is heated strongly with con.HCl	A greenish yellow gas is evolved.	Presence of Chromate
	No greenish yellow gas is evolved	Absence of Chromate.
A small amount of the mixture is heated gently with 2ml of con.Sulphuric acid.	A colourless gas which gives white dense fumes with a glass rod dipped in Ammonia.	Presence of Chloride.
	A reddish brown gas which turns fluorescein paper red is formed immediately.	Presence of Bromide

If no change is observed on gentle heating, heat the contents strongly.	A violet vapour which turns a fluorescein paper red is formed	Presence of Iodide
	A colourless gas which turns a moist glass milky with an oily appearance on the sides of test tube is formed.	Presence of Fluoride
	A reddish brown gas which turns Ferrous sulphate paper brown is formed	Presence of Nitrate.
	No characteristic change	Absence of Chloride, Bromide, Iodide, Fluoride adn nitrate.
5. Action of con.H_2SO_4 and MnO_2 A small amount of the substances taken in a test tube is heated strongly with 2ml con.Sulphuric acid and MnO_2.	A greenish yellow gas which turns a glass rod dipped in Silver nitrate, milky is produced.	Presence of Chloride
	A reddish brown gas which turns starch iodide paper blue is obtained and the solution in the test tube turns to a red liquid.	Presence of Bromide
	A violet vapour which turns a starch paper blue is obtained	

	and the solution in the test tube turns violet.	Presence of Iodide.
	No characteristic change is noticed	Absence Chloride, Bromide and Iodide.
A small amount of the mixture is heated strongly with con.Sulphuric acid in a test tube	A reddish brown gas which turns Ferrous sulphate paper brown is formed.	Presence of Nitrate
	No reddish brown gas is evolved	Absence of Nitrate
A small amount of the mixture is treated with 5ml of dil. Sulphuric acid and 1ml of 1% $KMnO_4$ solution and the change is noted in the cold	The pink colour is discharged in the cold	Presence of Arsenite and Ferrous salts.
If there is no change in the cold then heat the solution gently	The pink colour disappears while the solution turns red in colour	Presence of Bromide
	Pink colour disappears on heating only	Presence of Oxalate or Chloride.
	The pink colour is not discharge both in the cold and hot conditions	
A small amount of the mixture is dissolved in con.HNO_3 heating	An yellow precipitin is formed in the cold or on gentle warming	

and then this solution is transferred to 2ml of Ammonium molybdate solution	No precipitate is formed	Absence of Arsenite, Ferrous, Bromide, Oxalate and Chloride salts.
9. Ethyl borate test for Borate A small amount of the mixture taken in a test-tube is, mixed with 1ml of con. Sulphuric acid and 5 ml of Ethyl alcohol, boiled and then the escaping vapours are set fire	The vapours burn with a green edged flame The vapours doesnot burn with green edged flame	Presence of Phosphate or Arsenite Absence of Arsenite and Phosphate. Presence of Borate. Absence of Borate

C . Systematic Analysis of Acid Radicals

Preparation of Sodium carbonate extract.

About 2 gms of the mixture taken in a 100 ml beaker is mixed with thrice its weight of Sodium carbonate crystals and 15 ml of distilled water, boiled well for 15 minutes, cooled and then centrifuged. This centrifugate is called ‘the Sodium carbonate extract which must be tested as follows for the presence of certain acid radicals.

1. Test with $AgNO_3$ About 1 ml of the extract is neutralised with dil. HNO_3 with constant shaking, warmed to expell CO_2 evolved and then treated with a drop or two of Silver nitrate solution.	A curdy white precipitates formed which is soluble in excess of Ammonium hydroxide. A pale yellow precipitate which is sparingly soluble in Ammonia is formed	Presence of Chloride. Presence of Bromide

	An yellow precipitate insoluble in ammonia is formed	Presence of Iodide.
To the above solution or the filtrate if a precipitate is formed, add excess of Ammonia solution	An yellow ring is formed	Presence of Arsenite or Phosphate.
	A chocolate ring is formed	Presence of Arsenate
	No precipitate or a ring is formed	Absence of Chloride, Bromide, Iodide, Arsenite, Phosphate and Arsenate.
2. Barium chloride test. 1 ml of the extract is neutrilised with dil. HNO_3, as above, warmed and them treated with 1 ml of Barium chloride solution.	A white precipitate insoluble in con. HCl is formed.	Presence of Sulphate
	No white precipitate is formed	Absence of Sulphate.
3. Calcium chloride test. About 1 ml of the extract is neutralised by adding dil. Acetic acid in drops with constant shaking followed by the additiion of 5 drops of Calcium chloride solutiion.	A white precipitate is formed.	Presence of Oxalate or fluoride.

If a precipate is formed centrifuge it , dissolve it in dil. Sulphuric acid and then heated with a solution of dil. $KMnO_4$	The pink colour disappears.	Presence of Oxalate.
4. Brown ring test . To 1 ml of the extract dil. Sulphuric acid and freshly prepared Ferrous sulphate solution are added followed by the addition of con. Sulphuric acid through the sides of the test tube without shaking the solutiion.	The pink colour is not discharged	Presence of Fluoride
	No precipitate is formed	Absence of Oxalate and Fluoride.
	A brown ring is formed at the junction of the solutios.	Presence of Nitrate.
5. With H_2S. 2 ml of the extract is acidified withe dil. HCl and then passed H_2S gas through it.	No brown ring is formed	Absence of Nitrate
	An yellow precipitate is formed immediately	Presence of Arsenite.
		Presence of Arsenate
	An yellow precipitate is formed after a prolonged	Absence of Arsenite and Arsenate.

	treatement with H_2S. No precipitate even after passing H_2S for a long time.	

Confirmatory test for Acid Radicals

1. Chromyl chloride test for Chloride

1. A small amount of the given mixture is mixed with an equal amount of $K_2Cr_2O_7$ crystals, 1 ml of con. H_2SO_4 and heated strongly. The escaping vapours are collected in test tube containing a dilute solution of NaOH.	An yellow precipitate is formed	Chloride is confirmed
2. For Oxalate. A neutral solution of the mixture is treated with Ferrous sulphate solution	An yellow precipitate is formed	Oxalate is confirmed
3. a. For Phosphate . Magnesia mixture is added to the neutral solution of the mixture and then the sides of the test tube is scratched with a		

glass rod.	A white precipitate is formed	Phosphate is confirmed
b. $FeCl_3$ - test 1 ml of neutral $FeCl_3$ solution is added to the neutral solution of the mixture.	A reddish brown precipitate is formed	Phosphate is confirmed
4. For Arsenite. Scheel’s green test. Copper sulphate solution is added to 1 ml of the neutral solution of the mixture.	A scheel’s green precipitate is formed	Arsenite is confirmed
5. For Sulphate. 2ml of the Na_2CO_3 extract is neutralised withe dil.HNO_3 and then treated withe Lead acetate solution.	A white precipitate is formed	Sulphate is confirmed

D. SYSTEMATIC ANALYSIS OF BASIC RADICALS:

Elimination of Interfering Acid radicals (or) Preparation of Original Solution.

1. Elimination of Oxalate.

About 2 gms of the mixture is taken in a dry china dish and roasted for 15 to 30 minutes strongly. Then the roasted mixture is cooled, transferred to a boiling tube and dissolved by boiling with dil. HCl.

Then the solution is centrifuged and the precipitate if any is tested for the presence of I - group elements and the centrifugate is used for the II - and the further group analysis.

2. Eliminating of Fluoride (and Borate).

About 2 gms of the mixture is taken is boiling tube and con. HCl is added to it, till the acid covers completely the mixture and refluxed strongly till the whole of the acid evaporates. The residue is again covered with sufficient quantity of con. HCl and refluxed again as said above. This process is repeated not less than 4 - times.

Then the residue is cooled, dissolved in water, centrifuged and the precipitate if any is analysed for the group - I elements and the centrifugate is used for further group analysis.

3. Elimination of Arsenite. (This should be done after I - group but proceeding to the II - group).

The centrifugate obtained after the I - group is treated with H_2S where an yellow precipitate is formed. This precipitate is centrifuged and then H_2S is passed again the yellow precipitate is filtered. This process of passing H_2S and filtering the precipitate in continued till the solution doesnot give any more precipitate with H_2S.

The precipitate is analysed for the presence of II - group elements and the centrifugate is used for the III - and further group analysis.

4. Elimination Phosphate. (This should be done after II - group and before proceeding to the III - group.)

The centrifugate obtained after the precipitation of II - group elements is boiled well to expel the H_2S passed followed by the addition of excess of NH_4Cl solution and 1 ml of Zirconyl chloride (or nitrate). Now a white precipitate is formed and this must be centrifuged and discarded. Then Zirconyl chloride is added again and the precipitate is centrifuged and discarded. This process of adding Zirconyl chloride and discarding the precipitate is continued till the solution doesnot give any precipitate with Zirconyl chloride.

Now the centrifugate is used for the analysis of the III - and the further groups.

N.B.

If Oxalate, fluoride and Borate are present as the elimination radicals then the original solution can be prepared even at the beginning of the Basic radical analysis after eliminating these interfering radicals.

But if the interfering radical present are Arsenate and Phosphate then original solution must be prepared at the beginning and these radicals must be eliminated at the appropriate places. In such a condition the original solution must be prepared as detailed below.

Preparation of Original Solution.

The mixture is firstly dissolved in cold dil. HNO_3 and if not soluble then tried to dissolve by heating. If not soluble even in hot dil.HNO_3 then it must be tried in cold and then in con. HNO_3.

SEPARATION OF GROUPS

To the solution obtained after elimination or to the original solution dil. HCl is added and centrifuged if a precipitate is formed.

<table>
<tr><td>Residue</td><td colspan="4">Centrifugate</td></tr>
<tr><td rowspan="4">A residue is obtained Presence of I-group</td><td colspan="4">The above centrifuge is heated well to expel H_2S – gas and then 0.5mml of con.HNO_3 is added to followed by the addition of exdcess of Ammonium chloride solution and $NH_4 0H$ solution and centrifuged.</td></tr>
<tr><td rowspan="3">Residue
A residue is obtained Presence of III-group</td><td colspan="3">Centrifugate
To the above centrifugate H_2S gas is passed is obtaine and centrifuged.</td></tr>
<tr><td rowspan="2">Residue
A residue is obtained Presence of IV – group</td><td colspan="2">Centrifugate
The above centrifugate is boiled to expel H_2S and then NH_4Cl is added followed by $\left(NH_4\right)_2 CO_3$ solution.</td></tr>
<tr><td>Residue
A residue is obtained Presence of V-group</td><td>Centrifugate:
To the centrifugate is added Sodium hydrogen phosphate. A white precipitate is formed
Presence of VI – group.</td></tr>
</table>

GROUP ANALYSIS:

Analysis of I - group (Lead group).

TheI - group precipitate is boiled with 2 ml water and centrifuged even in the hot condition.

Residue.	Centrifugate:
No residue is obtained. Absence of Mercury and Silver.	On cooling a white precipitate is formed. This precipitate is again dissolved by boiling and the solution is divided in to two portions. 1. To one portion, Ammonium acetate solution is added followed by the addition of Potassium chromate solution. An yellow precipitate is formed . Presence of Lead. 2. To another portion of the solution KI - solution is added when an yellow precipitate is formed. This precipitate is boiled to dissolve and the solution is allowed to cool. Appearance of golden bangles is noticed. Presence of Lead is confirmed.

Analysis of group II - elements

Separation group II - in to group II A - and II B.

The II - group residue is washed well with water and then boiled with 2 ml of NaOH solution and then centrifuged.

Residue	Centrifugate:
A residue is obtained. Presence of II A – group elements	The centrifugate is neutralized with dil.HCl. A precipitate is formed. II B – group

Analysis of group II A - (Copper group)

The group II A - precipitate is washed well with water, dissolved in dil. Nitric acid and the centrifuged.

<table>
<tr>
<td rowspan="3">Residue :
No residue Absence of Mercury</td>
<td colspan="3">Centrifugate:
The centrifugate is treated with 1ml of dil.Sulphuric acid and centrifuged.</td>
</tr>
<tr>
<td rowspan="2">Residue
No residue Absence of Lead</td>
<td colspan="2">Centrifugate:
To the centrifugate an excess of NH_4OH solution is added and then centrifuged.</td>
</tr>
<tr>
<td>Residue
The residue is dissolved in dil. HCl and divided in to two portions.
1. One portion is added to 100ml of water in a beaker. A milky appearance is noted.
Presence of Bismuth.
2. To the another portion is added Sodium stannate solution.
A black precipitate is formed.
Presence of Bismuth.</td>
<td>Centrifugate:
If the centrifugate is blue in colour then it shows the presence of copper.
Divide the solution in to two portions and
1. To one portion add a small amount of CH_3COOH followed by Potassium ferro cyanide.Brown precipitate is formed.
2. To the other potion, H_2S gas is passed.
Yellow precipitate is formed.
Presence of Cadmium.</td>
</tr>
</table>

Analisis of II B group. (Tin goup)

The II B - group precipitate is digested with con. HCl for 10 minutes and then centrifuged.

Residue:	Centrifugate:
No residue Absence of Arsenic.	The centrifugate is divided in to two portions and tested as follows: 1. One portion, is heated with Zinc dust, filtered and then the filtrate is treated with Mercuric chloride solution. No silky white precipitate is formed. Absence of Tin. 2. The second portion is heated with Ammonium oxalate and then H_2S gas is passed. A red orange precipitate is formed. Presence of antimony.

Analysis of III - group. (Iron group)

The III - group precipitate is washed well with water, heated with Sodium peroxide (or Sodium hydroxide and Hydrogen peroxide) and then centrifuged.

Residue.	Centrifugate:
A residue shows the presence of Iron and Manganese. The residue is divided in to two portions and tested as follows. Test for Iron. One portion of precipitate is dissolved in dil. HCl and divided in to two portions. 1. To one portion Ammonium thiocyanate is added.	The centrifugate is divided in to two portions and to, 1. To one portion dil. HCl is added followed by the addition of excess of ammonium hydroxide solution. A white gelatinous precipitate is formed.

Blood red colour is formed. Presence of Iron. 2. To the other portion Potassium ferricyanide is added. A blue colour is formed. Presence of Iron. Test for Manganese. The other portion of the precipitate is boiled with Lead peroxide and con. HNO_3 diluted and then allowed to settle. A pink coloured solution is formed. Presence of Manganese.	Presence of Aluminium. 2. To the other portion, 1ml of dil. HCl, Ammonium acetate and 3 drops of Aluminon are added. A red precipitate is formed. Presence of Aluminium.

Analysis of IV - group (Zinc group).

The IV - group precipitate is washed well with water digested well with cold dil. HCl and then centrifuged.

<table>
<tr>
<td rowspan="2">Residue:
No residue is obtained.
Absence of Nickel and Cobalt.</td>
<td colspan="2">Centrifugate:
The centrifugate is boiled well to expel H_2S gas and then added excess of NaOH solution and centrifuged.</td>
</tr>
<tr>
<td>Residue:
The precipitate is treated with 2ml of dil.HNO_3 and a small amount of Sodium bismuthate heated gently and then allowed to stand.
Pink coloured solution is obtained.
Presence of Manganese.</td>
<td>Centrifugate:
The centrifugate is divided in to two portions and to.
1. One portion H_2S gas is passed.
2. To the other portion, CH_3COOH is added followed by the addition of Potassium ferrocyanide.</td>
</tr>
</table>

		A white precipitate is formed. Presence of Zinc.

Analysis of V - group (Calcium group).

The V - group precipitate is washed well with water and then dissolved in a minimum quantity of Acetic acid and then treated with 1 ml of Potassium chromate solution and centrifuged.

Residue.	Centrifugate:
An yellow residue is formed. Presence of Barium. The precipitate is made in to a paste with con. HCl and subjected in to flame test. An apple green flame is observed. Presence of Barium.	The centrifugate is re precipitated by treating with NH_4Cl solution and Ammonium carbonate solution. No precipitate shows the absence of Strontium and Calcium. If a precipitate is formed dissolve it in dil. Acetic acid and divide the solution in to two portions. 1. To one portion add a saturated solution of Calcium sulphate. A white precipitate is formed. Presence of Strontium. The precipitate on flame test gives a crimson red flame. Presence of Strontium. 2. To the other portion add Ammonium oxalate and Ammonium hydroxide solutions. A white precipitate is formed. Calcium is present. The precipitate when subjected to flame test gives a brick red flame. Calcium is confirmed.

Analysis of VI - group (Magnesium group).

To the centrifugate, obtained after the separation of the V - group elements, add Sodium hydrogen phosphate and the sides of the test tube must be scratched with a glass rod.

A white precipitate is formed.

Presence of Magnesium.

Test for Ammonium radical.

To 2 ml of the Nessler's reagent a pinch of the mixture is added and shaken well.

A reddish brown precipitate is formed.

Presence of Ammonium salts.

Result.

The given in - organic mixture contains,

-------------------- and ------------ as acid radicals

------------------- and ----------- as basic radicals.

2. INORGANIC PREPARATIONS.

1. PREPARATION OF SODIUM THIOSULPHATE.

Aim:

To prepare a maximum quantity of pure sample of Sodium thio sulphate penta hydrate. ($Na_2S_2O_3.5H_2O$) from the given simple salts.

Principle.

Sodium thio sulphate can readily be obtained by boiling a solution of Sodium sulphate with an excess of freely powdered Sulphur. The reaction taking place can be explained as follows.

Na_2SO_3 + S $Na_2S_2O_3 . 5H_2O$

Sodium sulphate Sodium thio sulphate.

Chemicals required.

i. Sodium sulphate --------------- 5 gm

ii. Sulphur --------------- 1 gm

Procedure.

5 gms of Sodium sulphate, taken in a 100 ml beaker in dissolved in 50 ml of water and then 1 gm of powdered Sulphur is added to it. Then the flask is fitted with an air condenser and refluxed until all the sulphur gets reacted.

The completion of the reaction is tested by placing a drop of reaction mixture on a litmus or phenolphthalein paper, which doesn't give a pink colour.

Then the solution is filtered and concentrated to 25 ml. Then on allowing the concentrated solution to cool without disturbing, crystals of sodium thio sulphate separates out.

If needed one or two crystals of Sodium thio sulphate may added for nucleation, that is to induce the crystalisation.

The crystals are filtered and dried over filter paper and the yield in noted.

Result.

The amount of Sodium thio sulphate obtained = -------- gms.

2. PREPARATION OF FERROUS AMMONIUM SULPHATE:

Aim.

To prepare the maximum yield of pure sample of Ferrous ammonium sulphate from the given salts.

Principle.

When the solutions of Ferrous sulphate and Ammonium sulphate are allowed to react, we get Ferrous ammonium sulphate as per the following chemical equation.

$$FeSO_4 + (NH_4)\ SO_4 + 6H_2O \quad SO_4.(NH4)\ .SO_4.$$

Chemicals required.

i. Ferrous sulphate ------ 5.0 gms

ii. Ammonium sulphate ------------- 2.5 gms

Procedure.

5 gms of Ferrous sulphate and 2.5 gms of Ammonium sulphate, taken in a 250 ml beaker is dissolved completely adding slowly, sufficient water, with constant stirring. Then a few drops of Con. Sulphuric acid is added to this to get a clear solution.

Then the solution is boiled for 5 minutes and allowed to crysatllise by standing. Now light blueish green crystals of Ferrous ammonium sulphate separates out.

Finally the crystals are filtered, dried and weighed to note the yield.

Result.

The amount of Ferrous ammonium sulphate obtained = ----- gms.

3. PREPARATION OF TETRAMINE COPPER (II) SULPHATE.

Aim.

To prepare a maximum yield of pure Tetramine copper (II) sulphate or Cuprammonium sulphate tetra hydrate from the given salts.

Principle.

When an excess of Ammonium hydroxide is added to a solution of Copper sulphate, a white precipitate formed first, gets dissolved again to give a deep blue solution of Cuprammonium sulphate complex. This complex is re precipitated from the solution by the addition of alcohol in which the it is insoluble.

The chemical reaction taking place can be represented as follows.

$$CuSO_4 + 4\,NH_4OH \qquad\qquad [\,Cu(NH_3)\quad]\,.SO4\,.\,4H_2O$$

Tetramine copper (II) sulphate.

Chemical required.

i. Copper sulphate -------------- 2.5 gm

ii. 1:1 Ammonia ----------- 5 ml

iii. Alcohol ------ 10 ml

Procedure.

2.5 grams of Copper sulphate taken in a100 ml beaker is dissolved in 10 ml of water, followed be the addition of few drops of Con. Sulphuric acid to get a clear solution. To this 1:1 Ammonium solution is added slowly with constant stirring till a clear blue solution is obtained. If a white precipitate or turbidity is persists, a little more of 1:1 Ammonia solution is to be added to get a clear solution.

Then 10 ml of Alcohol is added to this clear blue solution in drops with constant stirring when a purple precipitate of Cuprammonium sulphate is obtained. The beaker is heated on a water bath, to about 323k for 10 to 15 minutes to dissolve the precipitate. Now the solution is allowed to cool, when blue crystals of the complex chrysalises out.

The crystals are filtered at the pump, washed with alcohol, dried and finally the yield is noted.

Result.

The yield of Cuprammonium sulphate is = ------- gms.

4. PREPARATION OF COSMIC SALT;

Aim.

To prepare a maximum yield of pure sample of Micro cosmic salts from the given salts.

Principle.

When diSodium hydrogen phosphate is treated with a solution of Ammonium chloride, Micro cosmic salts will be formed as per the following chemical equation.

$$Na_2HPO4 + NH_4Cl \qquad\qquad Na(NH4)\ HPO_4 .\ 4H_2O + NaCl$$

Micro cosmic salt

Chemicals required.

1. Sodium hydrogen phosphate ------------- 6.5 gm.
2. Ammonium chloride ----------- 2.0 gm

Procedure.

6.5 gms of di sodium hydrogen phosphate taken in a 100 ml beaker is dissolved by boiling with 10 ml of water by constant stirring. Then to this solution 2 gm of Ammonium chloride is added, the solution concentrated by boiling and then allowed to coll without disturbing. Now crystals of micro cosmic salt separates out.

The crystals are separated by decantation, dried and then weighed to note the yield.

Result.

Amount of Microcosmic salt obtained = ------------- gms.

NOTES

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...