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UG TRB
CHEMISTRY
2023-2024

UNIT-1

ATOMIC STRUCTURE AND PERIODIC CLASSIFICATION & CHEMICAL BONDING

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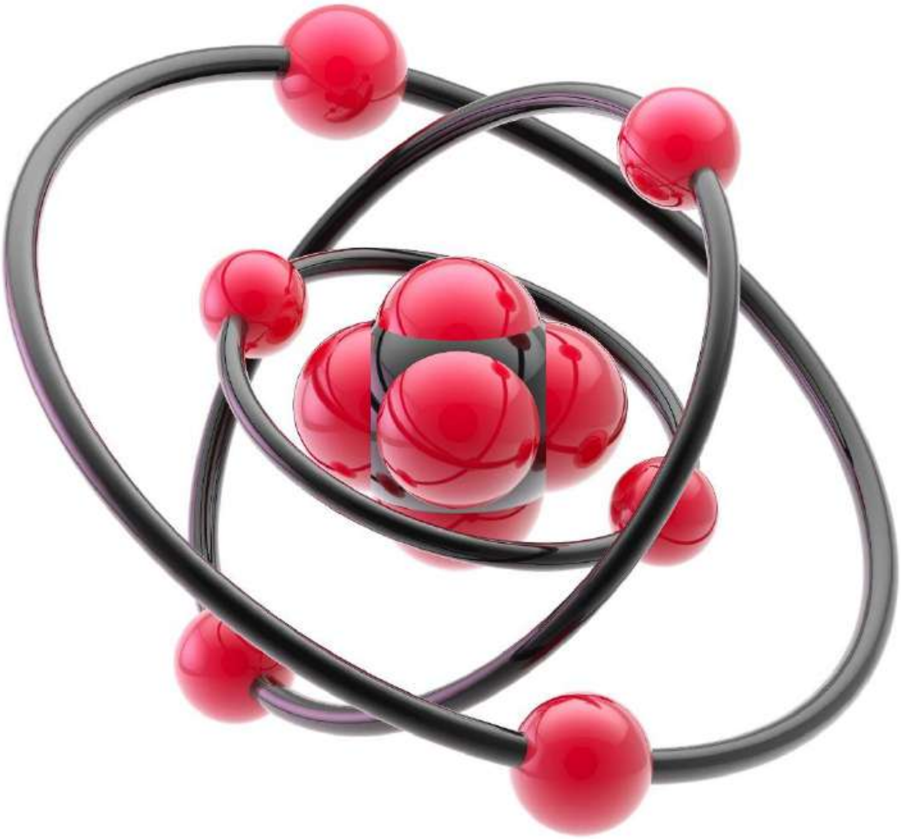
UNIT 1 – ATOMIC STRUCTURE



COMPETITIVE EXAM

For

UG TRB – 2023-24

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UG TRB – CHEMISTRY – 2023-24

UNIT 1

INORGNIC CHEMISTRY

ATOMIC STRUCTURE & PERIODIC CLASSIFICATION

1.1. INTRODUCTION

Atom is the Basic Component Some Basic Term About Atom is Given Below:

- The particles constituting an atom are the electron, the proton, and the neutron.
- An atom is composed of two regions: the nucleus, which is in the center of the atom and contains protons and neutrons, and the outer region of the atom, which holds its electrons in orbit around the nucleus.
- Protons and neutrons have approximately the same mass, about 1.67×10^{-24} grams, which scientists define as one atomic mass unit (amu) or one Dalton.
- Each electron has a negative charge (-1) equal to the positive charge of a proton (+1).
- Neutrons are uncharged particles found within the nucleus.
- The periodic table is a table that logically organizes all the known elements.
- Each row is named “period” where all of the elements have the same number of atomic orbitals.
- Each column is called “group” where the elements have the same number of electrons in the outer orbital.
- In this chapter will see more information about atomic structure and periodic classification

- Atoms are the extremely small particles that are the basic building blocks of ordinary matter.
- Atoms can join together to form molecules, which make up most objects. Different elements (e.g. oxygen, carbon, uranium) are made up of different types of atoms. An atom is the smallest unit of an element that will behave as that element.

1.1.1. Different Kinds of Atoms:

- Atoms, once thought to be the smallest building blocks of nature, are in fact made of smaller particles. Most often these particles are in balance, and as such the atom is stable and lasts nearly forever. Some atoms are out of balance. This can make them radioactive.
- Atoms are made of tiny particles called protons, neutrons and electrons. Protons and neutrons clump together to form a central nucleus. The electrons move in a cloud-like region around the nucleus.
- Stable: Most atoms are stable. Their protons, neutrons and electrons balance. Barring outside forces, a stable atom will stay the same indefinitely.
- Isotopes: Every atom is a chemical element, like hydrogen, iron or chlorine. Every element has cousins called isotopes. These have a different number of neutrons, but are otherwise the same. Having excess neutrons may make isotopes radioactive.
- Radioactive: Some atoms have too many neutrons in the nucleus, which makes them unstable. They're radioactive, giving off particles until they become stable.
- Ions: Atoms with extra or missing electrons are called ions. They have a positive or negative electric charge and are responsible for many chemical reactions.
- Antimatter: Every atomic particle has a twin anti-particle, with an opposite electric charge. Antimatter hydrogen atoms have been formed in the laboratory, containing an anti-proton and anti-electron. Antimatter is very rare and fragile.
- Atoms consist of an extremely small, positively charged nucleus surrounded by a cloud of negatively charged electrons. Although typically the nucleus is less than one ten-thousandth the size of the atom, the nucleus contains more that 99.9% of the mass of the atom. Nuclei are made of positively charged protons and electrically neutral neutrons held together by a nuclear force. This force is much stronger than the electrostatic force that binds electrons to the nucleus, but its range is limited to distances of the order of 1 x 10-15 meters. It is shown in the **Figure 1**.

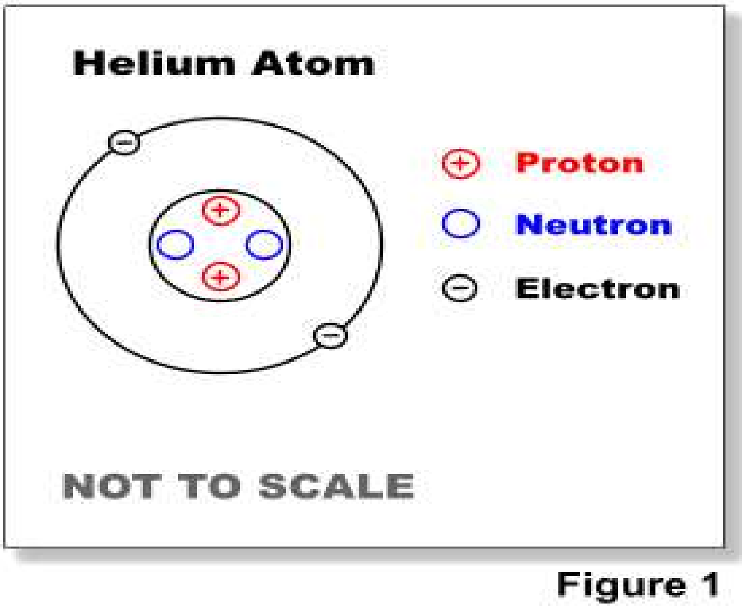

Figure 1: Representation of Helium atom

- The number of protons in the nucleus is called the atomic number (Z), the atomic number defines the element. The number of neutrons in the nucleus is denoted by N. The mass number (A) of the nucleus is equal to Z + N is shown in the **Figure 2**. The mass of the nucleus in atomic mass units (amu) is usually slightly different from the mass number.

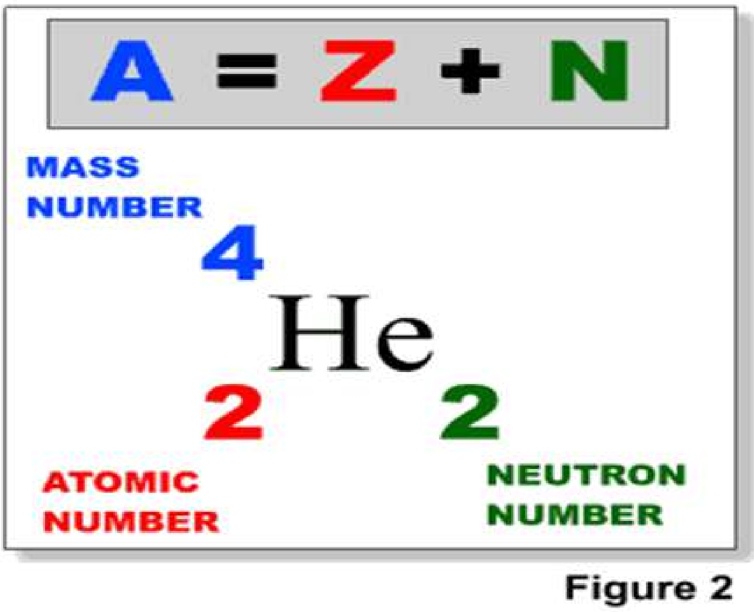

Figure 2: Pictorial representation of Mass Number

- Atoms of the same element can have different number of neutrons and they are called isotopes of that element. As an example, hydrogen has three (3) isotopes: hydrogen-1 (hydrogen), hydrogen-2 (deuterium) and hydrogen-3 (tritium) is shown in the **Figure 3.**

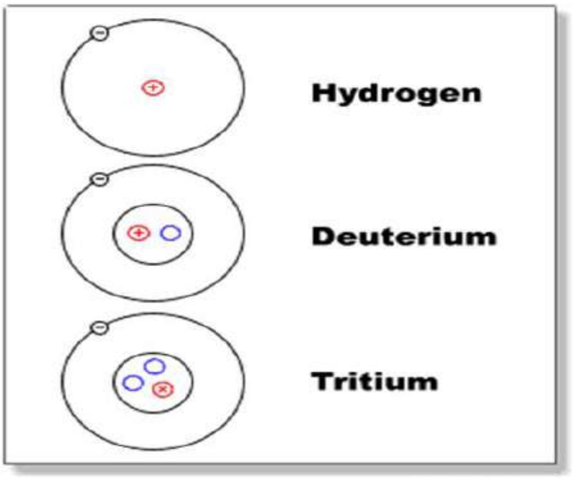

Figure 3

Figure 3: Indication of isotopes of Hydrogen

- At present there are 118 known elements which are typically displayed on the periodic table of the elements. Elements with atomic numbers 1 – 98 have all been shown to exist in nature while elements with atomic number 99 – 118 have only ever been produced artificially.
- Nuclides are often identified using the name of the element and the mass number (total number of protons and neutrons), i.e. lithiu-7, uranium-238, etc. **(Figure 4).**When referring to nuclides of the same element they are generally term isotopes i.e. uranium-238 & uranium-235. Radioactive nuclides or isotopes are called radionuclides or radioisotopes.

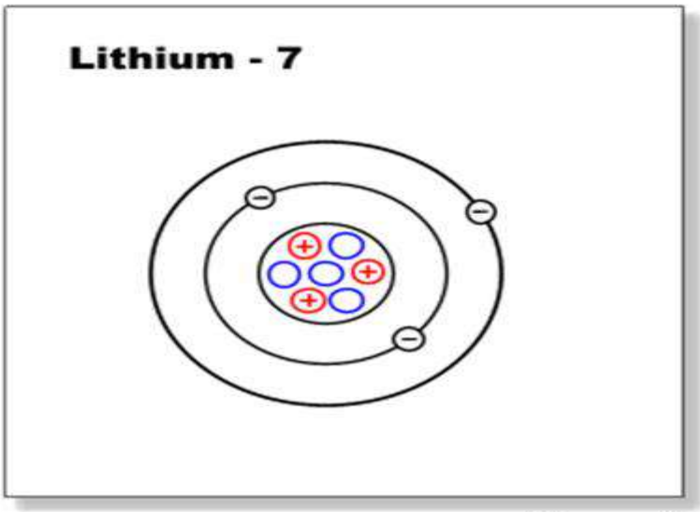

Figure 4

Figure 4: Indication of Lithium

- Among the elements there are 253 stable nuclides, and more than 3000 radioisotopes. The majority of the radioisotopes (>2400) are artificially produced and not presently found in nature.

1.2. ATOMIC STRUCTURE

- Atomic structure refers to the structure of an atom comprising a nucleus (centre) in which the protons (positively charged) and neutrons (neutral) are present. The negatively charged particles called electrons revolve around the centre of the nucleus is shown in the **Figure 5.**
- The history of atomic structure and quantum mechanics dates back to the times of Democritus, the man who first proposed that matter is composed of atoms. The study about the structure of an atom gives a great insight into the entire class of chemical reactions, bonds and their physical properties. The first scientific theory of atomic structure was proposed by John Dalton in the 1800s.
- The advances in atomic structure and quantum mechanics have led to the discovery of other fundamental particles.
- The discovery of subatomic particles has been the base for many other discoveries and inventions.
- The atomic structure of an element refers to the constitution of its nucleus and the arrangement of the electrons around it. Primarily, the atomic structure of matter is made up of protons, electrons and neutrons.
- The protons and neutrons make up the nucleus of the atom, which is surrounded by the electrons belonging to the atom. The atomic number of an element describes the total number of protons in its nucleus.

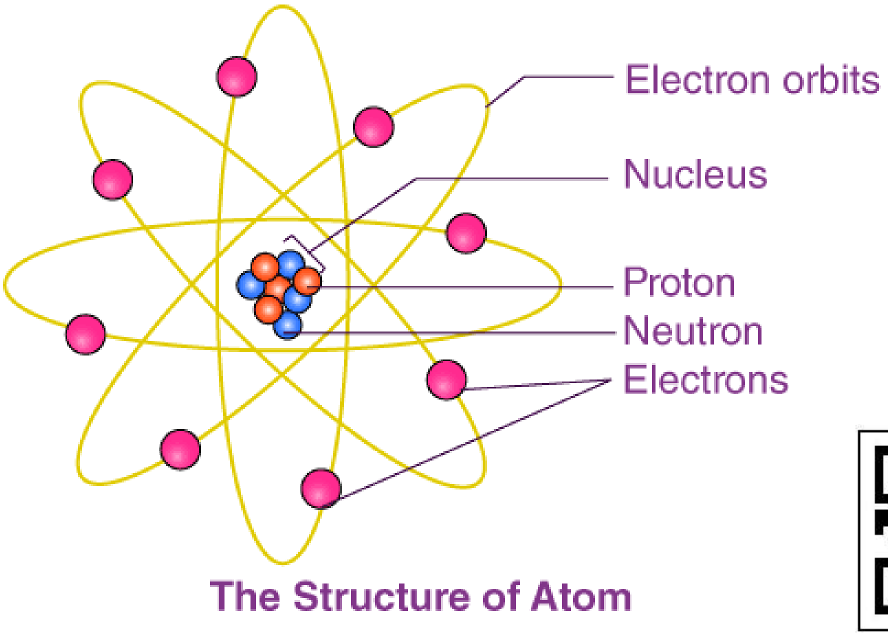

Figure 5: Pictorial representation of Structure of Atom

- The electron is by far the smallest: At 9.11 x 10-31 kg. It carries a negative electrical charge. Usually, it is bound to the positively charged nucleus due to the attraction created from the opposite electric charges. If the electrons carried by an atom are more or fewer than its atomic number, then the atom becomes respectively negatively or positively charged. A charged atom is known as an ion.
- Most of the mass of the atom comes from the protons and neutrons themselves, whereas electrons are almost 1/1837th times the weight of a proton or neutron. Protons and neutrons are both composed of other particles called quarks and gluons.
- The atomic number is the number of protons (equal to the number of electrons in a neutral atom) in the atom and the atomic mass number is the sum of the number of protons and neutrons in the atom.
- The atomic number (Z) is defined as the number of units of positive charges (protons) in the nucleus. It is the number of protons in the nucleus that determines the chemical properties of an atom.
- An atom may gain a positive or negative charge by either losing or gaining electrons respectively. Atoms may attach themselves to each other (of the same type or different type) to some atoms, the nucleus can change naturally. Such an atom is radioactive. In nature, there are some elements that are radioactive, like uranium or radium. In labs, scientists can produce radioactivity by bombarding atoms with smaller particles.
- The molecular mass of a substance is the sum of the atomic masses of all the atoms in a molecule of the substance. It is therefore the relative mass of molecule expressed in atomic mass units (u).
- Isotopes are atoms in a chemical element having different numbers of neutrons than protons and electrons. The atoms in a particular element have the same number of protons and electrons, but can carry varying numbers of neutrons.
- As instance, Hydrogen's atomic number is 1, i.e. its nucleus contains 1 proton. It also has one electron. The Hydrogen atom is neutral since it contains the same number of protons and electrons (as the positive and negative charges cancel each other out).
- However, approximately, one hydrogen atom out of 6000 contains a neutron in its nucleus. These atoms are still Hydrogen because they have one proton and one electron; they simply have a neutron that most hydrogen atoms do not carry. Hence, these atoms are called Isotopes.

- There’s also an isotope of hydrogen that contains two neutrons. It’s called Tritium, it doesn’t occur naturally on earth, but it can easily be created.rm molecules of different compounds, to form matter.

1.3. HISTORY OF THE PERIODIC LAW

- The early years of the 19th century witnessed a rapid development in analytical chemistry—the art of distinguishing different chemical substances—and the consequent building up of a vast body of knowledge of the chemical and physical properties of both elements and compounds.

- This rapid expansion of chemical knowledge soon necessitated classification, for on the classification of chemical knowledge are based not only the systematized literature of chemistry but also the laboratory arts by which chemistry is passed on as a living science from one generation of chemists to another. Relationships were discerned more readily among the compounds than among the elements; it thus occurred that the classification of elements lagged many years behind that of compounds. In fact, no general agreement had been reached among chemists as to the classification of elements for nearly half a century after the systems of classification of compounds had become established in general use.

- J.W. Döbereiner in 1817 showed that the combining weight, meaning atomic weight, of strontium lies midway between those of calcium and barium, and some years later he showed that other such “triads” exist (chlorine, bromine, and iodine [halogens] and lithium, sodium, and potassium [alkali metals]).

- J.-B.-A. Dumas, L. Gmelin, E. Lenssen, Max von Pettenkofer, and J.P. Cooke expanded Döbereiner’s suggestions between 1827 and 1858 by showing that similar relationships extended further than the triads of elements, fluorine being added to the halogens and magnesium to the alkaline-earth metals, while oxygen, sulfur, selenium, and tellurium were classed as one family and nitrogen, phosphorus, arsenic, antimony, and bismuth as another family of elements.

- Attempts were later made to show that the atomic weights of the elements could be expressed by an arithmetic function, and in 1862 A.-E.-B. de Chancourtois proposed a classification of the elements based on the new values of atomic weights given by Stanislao Cannizzaro’s system of 1858. De Chancourtois plotted the atomic weights on the surface of a cylinder with a circumference of 16 units, corresponding to the approximate atomic weight of oxygen. The resulting helical curve brought closely related elements onto corresponding points above or below one another on the cylinder, and he suggested in consequence that "the properties of the elements are the properties of numbers," a remarkable prediction in the light of modern knowledge.

1.4. CLASSIFICATION OF THE ELEMENTS

- In 1864, J.A.R. Newlands proposed classifying the elements in the order of increasing atomic weights, the elements being assigned ordinal numbers from unity upward and divided into seven groups having properties closely related to the first seven of the elements then known: hydrogen, lithium, beryllium, boron, carbon, nitrogen, and oxygen. This relationship was termed the law of octaves, by analogy with the seven intervals of the musical scale.
- Then in 1869, as a result of an extensive correlation of the properties and the atomic weights of the elements, with special attention to valency (that is, the number of single bonds the element can form), Mendeleyev proposed the periodic law, by which "the elements arranged according to the magnitude of atomic weights show a periodic change of properties." Lothar Meyer had independently reached a similar conclusion, published after the appearance of Mendeleyev's paper.

1.5. THE FIRST PERIODIC TABLE

- Mendeleyev's periodic table of 1869 contained 17 columns, with two nearly complete periods (sequences) of elements, from potassium to bromine and rubidium to iodine, preceded by two partial periods of seven elements each (lithium to fluorine and sodium to chlorine), and followed by three incomplete periods. In an 1871 paper Mendeleyev presented a revision of the 17-group table, the principal improvement being the correct repositioning of 17 elements. He, as well as Lothar Meyer, also proposed a table with eight columns obtained by splitting each of the long periods into a period of seven, an eighth group containing the three central elements (such as iron, cobalt, nickel; Mendeleyev also included copper, instead of placing it in Group I), and a second period of seven. The first and second periods of seven were later distinguished by use of the letters "a" and "b" attached to the group symbols, which were the Roman numerals.
- With the discovery of the noble gases helium, neon, argon, krypton, radon, and xenon by Lord Rayleigh (John William Strutt) and Sir William Ramsay in 1894 and the following years, Mendeleyev and others proposed that a new "zero" group to accommodate them be added to the periodic table. The "short-period" form of the periodic table, with Groups 0, I, II,III, IV, V, VI, VII VIII, became popular and remained in general use until about 1930.

UNIT I- Inorganic Chemistry and Chemical Bonding

1.54. Important Multiple-Choice Question:

1. The element having tetra atomic atomicity is

A) Helium B) Nitrogen C) Phosphorous D) Chlorine

2. Who was the first to propose Atomic theory?

A) J J Thomson B) Ruther ford C) John Dalton D) Neils Bohr

3. What is common among Lithium, Sodium and Potassium?

A) These have one electron in their outermost shell

B) There are alkaline earth metals

C) These cannot form oxides

D) These are inert elements

4. Which of the following statements does not form a part of Bohr's model of hydrogen atom?

A) Energy of the electrons in the orbit is quantized

B) The electron in the orbit nearest the nucleus has the lowest energy

C) Electrons revolve in different orbits around the nucleus

D) The position and velocity of the electrons in the orbit cannot be determined simultaneously

5. Identify the wrong statement in the following

A) The atomic radius of the elements increases as one moves down the first group of the periodic table

B) The atomic radius of the elements decreases as one moves across from left to right in the 2nd period of the periodic table

C) Amongst isoelectronic species, the smaller the positive charge on the cation, the smaller is the ionic radius

D) Amongst isoelectronic species, the greater the negative charge on the anion, larger is the ionic radius

6. Which of the following properties of atom could be explained correctly by Thomson Model of atom?

A) Overall neutrality of atom

B) Spectra of hydrogen atom

C) Position of electrons, protons and neutrons in atom

D) Stability of atom

7. The energy of an electron in first Bohr orbit of H-atom is –13.6 eV. The possible energy value of electron in the excited state of Li^{2+} is

A) – 122.4 eV B) 30.6 eV C) – 30.6 eV D) 13.6 eV

8. Electronic configuration of the outer shell of the element Gd with atomic number 64 is

A) $4f^4\ 5d^5\ 6s^1$ B) $4f^3\ 5d^5\ 6s^2$ C) $4f^5\ 5d^4\ 6s^1$ D) $4f^7\ 5d^1\ 6s^2$

9. If both the K and L shells are full, what would be the atomic number of that element?

A) 20 B) 14 C) 10 D) 16

10. Which of the following statements about the electron is incorrect?

A) It is a constituent of cathode rays

B) The mass of an electron is equal to the mass of a neutron

C) It is a basic constituent of all atoms

D) It is a negatively charged particle

11. The ratio of the amplitude of the magnetic field to the amplitude of the electric field for electromagnetic wave propagation in a vacuum is equal to

A) Unity

B) Speed of light in vacuum

C) Reciprocal of the speed of light in vacuum

D) The ratio of magnetic permeability to electrical susceptibility in a vacuum.

12. Which properties amount the following is false about electromagnetic waves?

A) The energy in an electromagnetic wave is divided equally between electric and magnetic vectors.

B) Both electric and magnetic field vectors are parallel to each other and perpendicular to the direction of propagation of the wave.

C) These waves do not require any material medium for propagation

D) Both electric and magnetic field vectors attain the maxima and minima at the same place and the same time

13.To which part of the spectrum does an EM wave belong if the energy of the wave is of the order of 15 KeV.

A) X rays B) Infrared rays C) Ultraviolet rays D) Gamma rays

14. The ultra-high frequency band of radio waves in the electromagnetic wave is used as in

A) Television B) Cellular phone communication

C) Commercial FM radio D) Both a and b

15. Good absorber of heat is good radiator of heat also is

A) Stefan's law B) Kirchhoff's law C) Planck's law D) Wien's law

16. A man with dark skin, in comparison with a man with white skin, will experience

A) Less heat and less cold B) Less heat and more cold

C) More heat and less cold D) More heat and more cold

17. Each object emits radiation. The radiation energy is proportional to what power of temperature?

A) T B) T^2 C) T^3 D)T^4

18. A polished metal plate has a rough and black spot. It is heated to 1400K and brought immediately in a dark room. Which of the following is true?

A) The spot will appear brighter than the plate

B) The spot will appear darker than the plate

C) The spot and plate will appear equally bright

D) The spot and the plate will not be visible in the dark room

19. A black body is at a temperature of 500K.It emits energy at a which is proportional to

A) $(500)^4$K B) $(500)^3$ K C) $(500)^2$ K D) (500) K

20. Electromagnetic wave theory of light could not explain Black Body radiations.

A) True B) False

C) Sometimes true sometimes false D) Neither true nor false

21. **Assertion:** Photoelectric effect demonstrates the wave nature of light.

Reason: The number of photoelectrons is proportional to the frequency of light

A) If both assertion and reason are true and the reason is the correct explanation of the assertion

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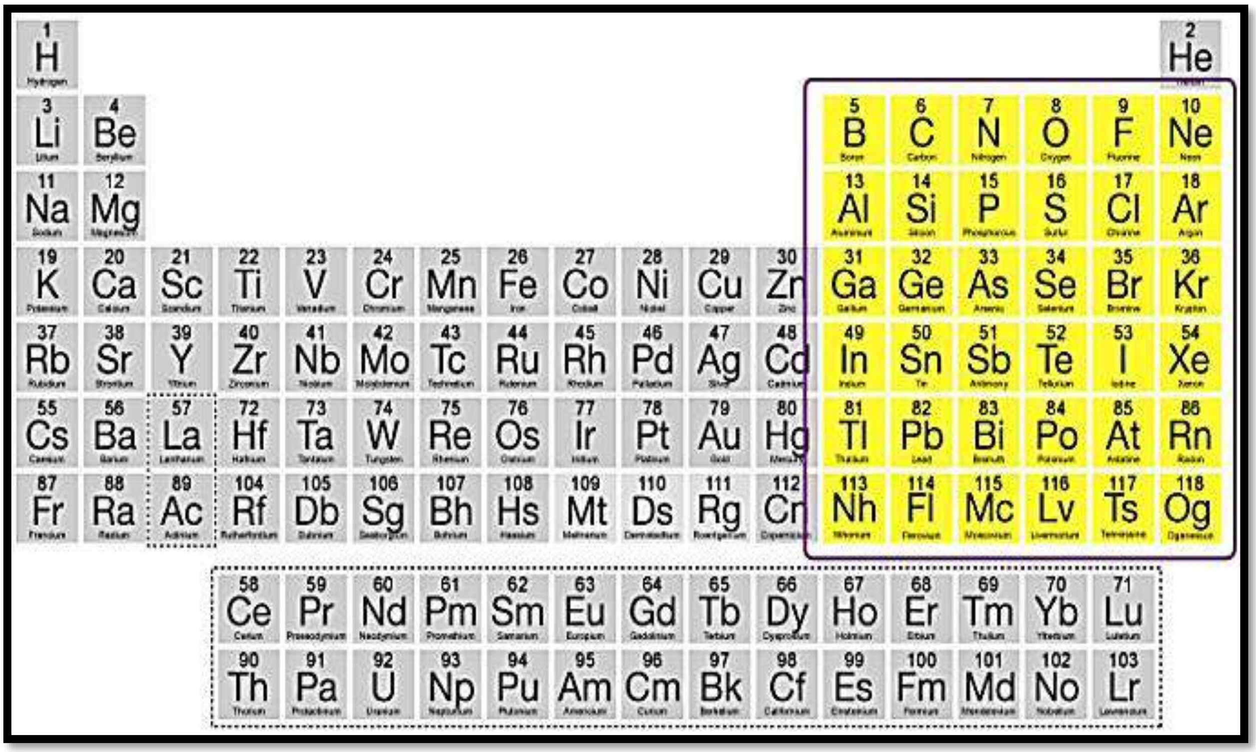
INORGNIC CHEMISTRY - UNIT 2

'p, d and f' Block Elements

2.1. p- Block Elements:

- p- block elements are those in which the last electron enters any of the three p-orbitals of their respective shells. Since a p-subshell has three degenerate p-orbitals each of which can accommodate two electrons, therefore in all there are six groups of p-block elements.
- p-block elements are shiny and usually a good conductor of electricity and heat as they have a tendency to lose an electron. You will find some amazing properties of elements in a p-block element like gallium. It's a metal that can melt in the palm of your hand. Silicon is also one of the most important metalloids of the p-block group as it is an important component of glass.
- p- block elements are nothing but the element in which the last electron enters the outermost p-subshell. P block starts from the 13th group and goes till the 18th group in the periodic table is shown in the **Figure 1.**
- Coal is used in villages to cook food. It is nothing but a p-block element i.e., carbon. diamonds used for making beautiful ornaments are also made up of carbon. Aluminium foil made up of aluminium is also made up of the p-block element.
- The p-block is the region of the periodic table that includes columns IIIA to column VIIIA and does not include helium. There are 35 p-block elements, all of which are in p orbital with valence electrons. The p-block elements are a group of very diverse elements with a wide range of properties.



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

- The elements p-block are so-called because their valence electrons are filled in an orbital p. These are often called Standard Components, in order to differentiate them from the sequence of transformation and internal transformation.
- Non-metals are on the extreme right side of the periodic table, except for hydrogen, found in the upper left corner. The 17 non-metal elements are: Hydrogen, Helium, Carbon, Nitrogen, Oxygen, Fluorine, Neon, Phosphorus, Sulphur, Chlorine, Argon, Selenium, Bromine, Krypton, Iodine, Xenon, and Radon.
- Usually non-metal is brittle when it is solid and typically has low thermal conductivity and electrical conductivity. Chemically, non-metals tend to have relatively high energy from ionization, contact with electrons, and electron negativity. As they react with other elements and chemical compounds, they receive or exchange the electrons.
- The general electronic external configuration for p-block components is $ns^2\ np^{(1-6)}$.
- The property of p-block element that gives it the ability to form covalent bonds with other atoms of same element (resulting in the formation of a chain of atoms) is called catenation. Carbon exhibits the property of catenation to a great extent. For example, carbon atoms can combine to each other to form long chains, branched chains and closed rings.
- In p-block elements, a lot of variation in properties of elements in a group is observed. Because, difference in inner core of electronic configuration greatly influences the physical and chemical properties of elements.

2.1.1. Occurrence of the p-Block Elements:

- Some elements occur free as well as in the combined state in nature. For example, elements such as oxygen, nitrogen, carbon, sulphur occur in both the form. Noble gases occur in free state only. All other elements usually occur in combined state.

2.1.2. General characteristics of p-block Elements:

2.1.2.1. Electronic Configuration:

The general electronic configuration of p-block elements is $ns^2 np^{1-6}$.

1) These elements include metals and non-metals with a few semi metals (Metalloids).
2) Most of them form covalent compounds.
3) These elements possess relatively higher ionization energy and the value tends to increase along the period but decrease down the group.
4) Most of the elements show negative (except some metals) as well as positive oxidation states (except Fluorine).
5) One of the familiar characteristics of p-block elements is to show inert pair effect i.e. the tendency of being less availability for ns electron in bonding. The inert pair effect increases down the group with the increase in atomic number.

2.1.2.2. Group 13 Elements - The Boron Family:

The group 13(IIIA) elements are Boron, aluminium, gallium, indium and thallium.

1) Boron is a relatively rare element, accounting for only about 0.001% of the earth's crust by mass.
2) Aluminium is the most important of 13th group elements.
3) Gallium is remarkable for its unusually low melting point (29.7°C) and therefore generally exist as a liquid at room temperature. Its most important use is in making gallium arsenide. This is a semi conductor material employed in the manufacture of diode lasers for laser printers, compact -disc players and fibre optic communication devices.
4) Indium is also used in making semi-conductor devices, such as transistors and electrical resistance thermometers called thermistors.
5) Thallium is extremely toxic and has no commercial use.

i) Boron:

- It has Atomic Number of 5 and the Electronic Configuration is given as: [He] $2s^2 2p^1$.   It belongs to Group Number: 13 and   Period Number: 2

ii) Aluminium:

- It has Atomic Number of 13 and the Electronic Configuration is given as [Ne] 3s2 3p1. It belongs to Group Number: 13 and Period Number: 3

iii) Gallium:

- It has Atomic Number of 31 and the Electronic Configuration is given as [Ar] $3d^{10}$ $4s^2$ $4p^1$. It belongs to Group Number: 13 and Period Number: 4

iv) Indium:

- It has Atomic Number of 49 Electronic Configuration is given as [Kr] $4d^{10}$ $5s^2$ $5p^1$. It belongs to Group Number: 13 and Period Number: 5

v) Thallium:

- It has Atomic Number: 81 and the Electronic Configuration is given as [Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^1$. It belongs to Group Number: 13 and Period Number: 6

2.2. Some Important Special Characteristics of p-block Elements:

1. Boron, carbon, nitrogen, oxygen, fluorine and neon head these groups of p block elements. Their valence shell electronic configuration is ns2 np1-6 where n= 2-7.
2. The maximum oxidation state shown by a p block element is equal to the sum of the valence electrons or the group number minus 10. This is called group oxidation state. Beside group oxidation state, p block elements show a number of other oxidation states.
3. In boron, carbon and nitrogen families, the group oxidation state is the most stable for the lighter elements in the group. A lower oxidation state which is 2 units less than the group oxidation state becomes progressively more stable for the heavier elements in each group.
4. The group oxidation state of group 13 elements is +3 but +1 oxidation state is most stable for thallium. The group oxidation state for group 14 elements is +4 but +2 oxidation state is most stable for lead.

Trend of occurrence of oxidation state two units less than the group oxidation state is called inert pair effect and becomes more prominent as we move down the group.

2.2.1. Chemical Behaviour:

1. p-block is the only one which contains metals, non-metals and metalloids. The common metal among p block elements is: aluminium, gallium, indium and thallium (group 13), tin and lead (group 14) and bismuth (group 15). The common metalloids are silicon, germanium, arsenic, antimony and tellurium while all the remaining elements are non-metals.

2. Non-metals have higher ionization enthalpies and higher electronegativity than those of metals. Therefore, non-metals readily form anions.

3. The compounds formed by the union of highly reactive metals with non-metals are generally ionic because of large differences in their electro negativities.

- Compounds formed by the union of non-metals themselves are largely covalent in character due to small differences in their electronegativities. Oxides of non-metals are either acidic or neutral; the oxides of metals are always basic in nature.
- More electropositive the metal, the more basic is its oxide and more electronegative the non-metal, more acidic is its oxides. Among p-block elements, the acidic character of the oxides increases or basic character decreases along a period. The basic character of oxide increases or the acidic character decreases down the group.
- First member of each group of p block elements differ from its exceeding members of their respective group.

The two main reasons for the differences are:

1. Size and other properties which depends upon size.
2. Absence of d orbital in their valence shell.

2.2.2. Size and other Properties Which Depend Upon Size:

- Due to small size, high electronegativity and high ionization enthalpy, the first element of each group of p-block elements differs from rest of the members of the respective groups.

2.2.3. Absence of d-Orbital:

- The absence of d-orbitals in the elements of 2nd period and the presence of d orbital in the heavier elements.

a) Maximum Covalency of Four:

- The first member of each group has 4 orbitals in the valence shell for bonding and hence can accommodate at the maximum 4 pairs or 8 electrons. These elements show a maximum covalency of four. Elements of 3rd period of p-block elements have vacant 3d orbitals lying between 3p and 4s level of energy. Using these d-orbitals, the elements of 3rd period can accommodate more electrons and hence can expand their covalency beyond 4.

1) Boron forms only $[BF_4]^-$ or $[BH_4]^-$ ion while Al gives $[AlF_6]^{3-}$ ion.

2)Carbon forms only tetrahalides whereas other members form hexahalides, i.e. $[SiF_6]^{2-}$, $[GeCl_6]^{2-}$, $[SnCl_6]^{2-}$.

3) Nitrogen forms only NF_3 while phosphorus forms both trihalides i.e., PF_3, PCl_3 and pentahalides i.e., PF_5 and PCl_5.

4) Fluorine does not form FCl_3 having 10 valence electrons while chlorine forms ClF_3.

b) Reactivity:

- Due to presence of d orbital, the elements of 3rd period are more reactive than elements of 2nd period which do not contain d-orbitals.
- Tetrahalides of carbon are not hydrolyzed by water while tetrahalides of other elements of group 14 are readily hydrolyzed. This hydrolysis involves the nucleophilic attack by water molecules and the pair of electrons provided by water is accommodated in the vacant d-orbitals.

c) Tendency to form Multiple Bonds:

1. The presence of d-orbitals also influences the chemistry of heavier elements in a number of other ways.
2. The combined effect of size and availability of d-orbital affects the ability of these elements to form π-bonds.
3. The first member of each group differs from the heavier elements in its ability to form pπ-pπ multiple bonds either with itself or with the other elements of the second period. This type of π-bonding is not strong in case of heavier p-block elements. The heavier elements also form π-bonds but this involves d-orbitals.

- For Example: In SO_2, one of the two π-bonds between S and O involves dπ-pπ bonding while the other involves pπ-pπ bonding. In SO_3 two of the three π-bonds involved dπ-pπ bonding while the third one involves pπ-pπ bonding. In these dπ-pπ bonds, a half filled 3d orbital of sulphur overlaps with the half-filled 2p orbitals of oxygen.
- Since d -orbitals are of higher energy then p-orbitals; therefore, they contribute less towards the overall stability of the molecule as compared to pπ-pπ bonding

between elements of 2nd period. But at the same time, such type of bonding may increase the coordination number in species of heavier elements in the same oxidation state.

2.3. Position of p-block Elements in the Periodic Table:

- In the elements of p-block, the last electron enters the furthest p orbital. They have 3 to 8 electrons in the peripheral shell. As we realize that the quantity of p orbitals is three and, therefore, the most extreme number of electrons that can be obliged in an arrangement of p orbitals is six. Consequently, there are six groups of p-block elements in the periodic table numbering from 13 to 18.

  I. First group: group IIIA called as Boron group
  II. Second group: group IVA called as Carbon group
  III. Third group: group VA called as Nitrogen group
  IV. Fourth group: group VIA called as Chalcogens
  V. Fifth group: group VIIA called as Halogens
  VI. Sixth group: zero group or group 18 called as Inert or Noble gasses group.

- In the p-block, all the three sorts of elements are available, i.e. the Metals, Non-Metals, and Metalloids. The crisscross line in the p-block isolates every one of the elements that are metals from those that are non-metals. Metals are found on the left of the line, and non-metals are those on the right. Along the line, we discover the metalloids. Because of the nearness of a wide range of elements, the p-block demonstrates a great deal of variety in properties.
- You must have seen that coal is used in villages to cook food. It is nothing but a P-block element i.e., carbon. Diamonds used for making beautiful ornaments are also made up of carbon. Aluminium foil made up of aluminium is also made up of the p block element.

2.3.1. Electronic Configuration of p-Block Elements:

- The general electronic configuration of p-block elements is ns^2np^{1-6}(except He). Whereas the inner core electronic configuration may differ. Just because of this difference in the inner core, there are changes in both physical and chemical properties of the elements.

- The general electronic configuration appeared by elements from group13 to 18 of p-block is as given underneath: -
    - Group 13 (Boron family):- $ns^2 np^1$
    - Group 14 (Carbon family):- $ns^2 np^2$
    - Group 15 (Nitrogen family):- $ns^2 np^3$
    - Group 16 (Oxygen family):- $ns^2 np^4$
    - Group 17 (Halogen family):- $ns^2 np^5$
    - Group 18 (Noble gases):- $ns^2 np^6$ (except Helium)
- The general electronic configuration of Helium is $1s^2$. Because of their particular electronic configuration p-block elements demonstrate a great deal of variety in properties.
- The oxidation state of elements in p – block is maximum when it is equal to a total number of valence electrons i.e., the sum of S and P electrons. One of the most interesting facts about the p-block elements is that it contains both non-metals and metalloids.

2.4. Silicones - Structure and Uses:

- The silicones are a group of organosilicon polymers. They have a wide variety of commercial uses.
- The complete hydrolysis of $SiCl_4$ yields silica SiO_2, which has a very stable three-dimensional structure. The fundamental research of F.S. Kipping on the hydrolysis of alkyl-substituted chlorosilanes led, not to the expected silicon compound analogous to a ketone, but to long-chain polymers called silicones is shown in the **Figure 2.**

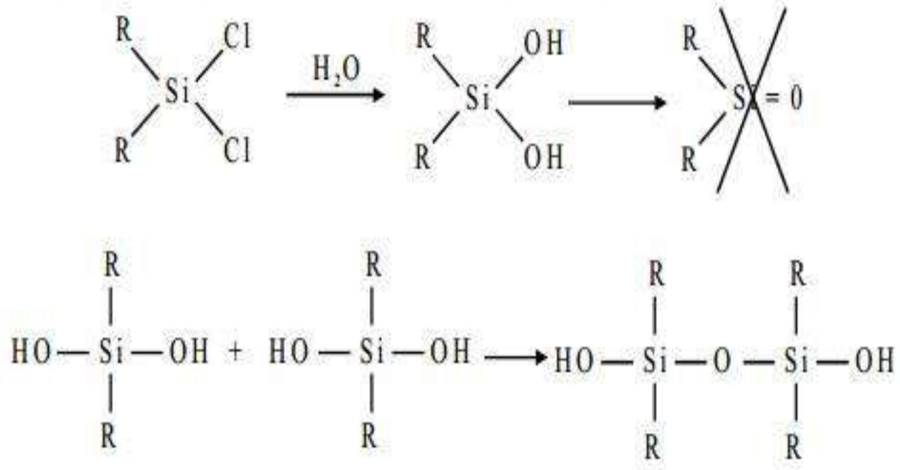


Figure 2: Structure of silicones

- The starting materials for the manufacture of silicones are alkyl-substituted chlorosilanes. Thus, the hydrolysis of trialkylmonochlorosilane R_3SiCl yields hexa- alkyl siloxane is shown in the **Figure 3.**

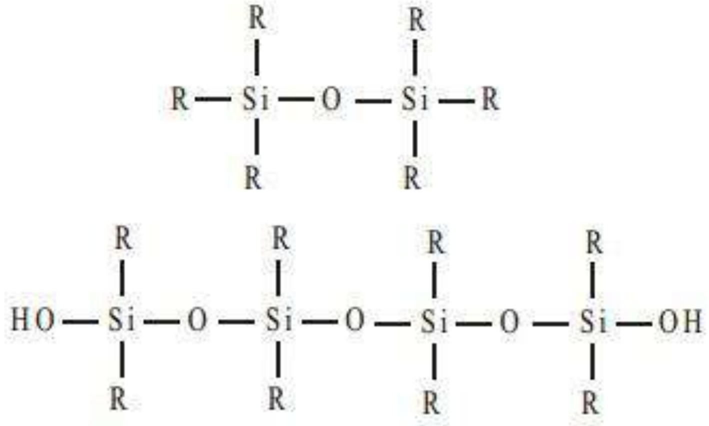


Figure 3: Structure of hexa-alkyl siloxane

- The dialkyldichlorosilane R_2SiCl_2 on hydrolysis gives rise to straight chain polymers and, since an active OH group is left at each end of the chain, polymerization continues and the chain increases in length.
- The hydrolysis of alkyl trichlorosilane $RSiCl_3$ gives a very complex cross- linked polymer. Illustration of cross-linked polymer is given in the **Figure 4.**

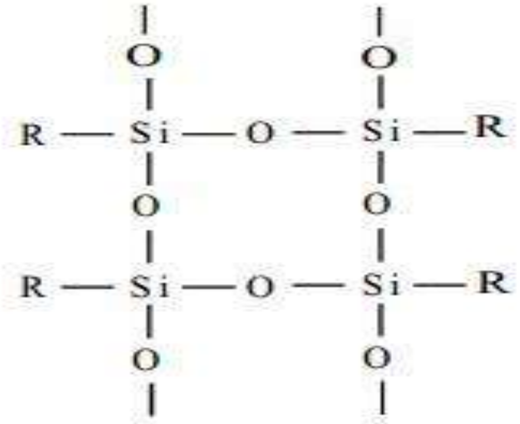


Figure 4: Illustration of cross-linked polymer

2.5. Anomalous Nature of Fluorine:

- Fluorine is the most reactive element among halogen. This is due to the minimum value of F-F bond dissociation energy.Fluorine decomposes cold dilute alkalis liberating OF_2 and with conc. alkali, O_2 is liberated. Under similar conditions, the other halogens will give rise tothe hypohalites and halates respectively.

2.38. UNIT II (p-block elements) – Important Multiple-Choice Questions:

1. What is the correct order of electron affinity among O, F and Cl?

A) O < Cl < F B) O < F < Cl C) F < O < Cl D) Cl < O < F

2. A yellow precipitate is formed upon the addition of aqueous silver nitrate to a solution of?

A) Orthophosphate B) Metaphosphate

C) Pyrophosphate D) Phosphite

3. Which among these has the highest bond angle?

A) NH_3 B) NF_3 C) BF_3 D) PH_3

4. How many S-S bonds are there in tetrathionate ion?

A) 2 B) 3 C) 4 D) 5

5. H_2S is more acidic than H_2O because

A) Oxygen is more electronegative than sulphur

B) Atomic number of sulphur is higher than oxygen

C) H — S bond dissociation energy is less as compared to H — O bond

D) H — O bond dissociation energy is less also compared to H — S bond

6. Helium is preferred to be used in balloons instead of hydrogen because it is

A) Incombustible B) Lighter than hydrogen

C) More abundant than hydrogen D) Non-polarizable

7. Among the 15th group elements, as we move from nitrogen to bismuth, the pentavalency becomes less pronounced and trivalency becomes more pronounced due to

A) Nonmetallic character B) Inert pair effect

C) High electronegativity D) Large ionization energy

8. **Assertion:** In p-block elements, a lot of variation in properties of elements in a group isobserved.

Reason: Difference in inner core of electronic configuration greatly influence the physical and chemical properties of elements

A) Both assertion and reason are correct and the reason is the correct explanation of the assertion

B) Both assertion and reason are correct and the reason is not the correct explanation of the assertion

C) Assertion is correct but the reason is incorrect

D) Both assertion and reason are incorrect

9. Ionic radii (in Å) of As^{3+}, Sb^{3+} and Bi^{3+} follow the order

A) $As^{3+} > Sb^{3+} > Bi^{3+}$ B) $Sb^{3+} > Bi^{3+} > As^{3+}$

C) $Bi^{3+} > As^{3+} > Sb^{3+}$ D) $Bi^{3+} > Sb^{3+} > As^{3+}$

10. Nitrogen is relatively inactive element because

A) Its atom has a stable electronic configuration

B) It has low atomic radius

C) Its electronegativity is fairly high

D) Dissociation energy of its molecule is fairly high

11. Pick out the wrong statement.

A) Nitrogen has the ability to form pπ-pπ bonds with itself

B) Bismuth forms metallic bonds in elemental state

C) Catenation tendency is higher in nitrogen when compared with other elements of the same group

D) Nitrogen has higher first ionisation enthalpy when compared with other elements of the same group

12. The type of hybridization of boron in diborane is?

A) sp^3 hybridization B) sp^2 hybridization

C) sp hybridization D) sp^3d^2 hybridization

13. AlF_3 is soluble in HF only in presence of KF. It is due to the formation of?

A) $K_3[AlF_3H_3]$ B) $K_3[AlF_6]$ C) AlH_3 D) $K_3[AlF_3H]$

14. Boron compounds behave as Lewis acids, because of their

A) Ionization property B) Electron deficient nature

C) Acidic nature D) Covalent nature

15. Collectively the elements of group 15 are called –

A) Pnicogens B) Pnicopens C) Nicopen D) None of these

16. Boric acid is an acid because its molecule

A) Contains replaceable H^+ ion

B) Gives up a proton

C) Accepts OH^- from water releasing proton

D) Combines with proton from water molecule

17. Which of the following structure is similar to graphite?

A) B_4C

B) B_2H_6

C) BN

D) B

18. **Assertion (A):** When diborane is heated with NH_3 200^0 C, borazole is obtained.

Reason (R): Borazole is known as inorganic benzene.

A) Both A and R is true and R is correct

B) Both A and R is true and R is not correct

C) A is true but R is false

D) a is false but R is true

19. Alum results in early sedimentation true or false?

A) True

B) False

C) Sometimes true sometimes false

D) Neither true nor false

20. Which of the following is not a common property of aluminium alloys?

A) Low strength

B) Heat treatable

C) Easy for machining

D) Readily joined b welding

21. Why has the aluminium association established a system of designating aluminium alloys?

A) To create employment

B) To remove confusion

C) To encourage research

D) To ensure availability

22. Aluminium alloys also have a system that indicates temper.

A) True

B) False

C) Sometimes true sometimes false

D) Neither true nor false

23. Which of the following is the chemical formula of fullerenes?

A) C_0

B) C_6

C) C

D) C_{60}

24. Stainless steel is very useful material for our life. In stainless steel, iron is mixed with

A) Ni and Cr

B) Cu and Cr

C) Ni and Cu

D) Cu and Ni

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UG TRB
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UNIT-3
COORDINATION CHEMISTRY, NUCLEAR CHEMISTRY & ANALYTICAL CHEMISTRY

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II. NUCLEAR CHEMISTRY

III. ANALYTICAL CHEMISTRY

UG TRB – CHEMISTRY – 2023-24

INORGANIC CHEMISTRY - UNIT 3

Co-Ordination Chemistry, Nuclear Chemistry & Analytical Chemistry

I. CO-ORDINATION CHEMISTRY

3. Coordination Compound:

- Special class of substances with chemical structures in which a central metal atom is surrounded by nonmetal atoms or groups of atoms, called ligands, joined to it by chemical bonds.
- In which ligand give the electron and central metal take the electron.
- Generally, results from the combination of two or more stable species and retain their identity in solid as well as in solution phase (in ionic or aqueous solution)

For Example –

$$4KCN + Fe(CN)_2 \rightarrow K_4\left[Fe(CN)_6\right]$$

- When $K_4\left[Fe(CN)_6\right]$ is dissolved in aqueous solution or ionic salt then it dissolve in ionic form and give 4K$^+$ and $\left[Fe\ (CN)_6\right]_4^-$ But when $\left[Fe\ (CN)_6\right]_4^-$ is dissolved in water it does not lose its identity means does not give Fe^{2+} and CN$^-$.
- This $\left[Fe(CN)_6\right]_4^-$ is called coordinated complex ion.
- Generally, when solution of two or more simple stable salts are mixed together in simple molecular proportion and the obtained solution is allowed to evaporate, crystals of a new compound are obtained.

- This new compound is called addition compound. These addition compound maybe doubles alt and coordination complex.

Simple Compounds Addition Compounds

$KCl + MgCl_2 + 6H_2O \rightarrow KCl.MgCl_2.6H_2O$

Carnallite

$Fe(CN)_2 + 4KCN \rightarrow Fe(CN)_2.4KCN$

Potassium ferrocyanide

- In above examples one of them represents addition compound and other is an example of coordination compound.

Difference between Coordination complexion and Double salt

Double Salt	Coordination Compound
1. Exist only in solid state in solution phase, in liquid phase it generally dissociate.	1. retain their identity in solid phase as well as in liquid phase or aqueous phase
2.Their property are same as the property of constituents species	2.their property are different as their constituent species
3.In doubles alt Metalion exhibit their Normal Valency	3 In coordination compound number of the ion or molecule surrounded by metal ion are beyond its.
4. When carnallite $KCl.MgCl_2.6H_2O$ is dissolved in water the aqueous solution of $KCl.MgCl_2.6H_2O$ gives the tests of K^+, Mg^{2+}, and Cl^- ions.	4.When $K_4Fe(CN)_6$ is dissolved in water then it give $4K^+$ and $[Fe\ (CN)6]^{4-}$. Does not give the test of Fe^{2+} and CN^-

Representation of coordination compound

$$K_4\left[Fe(CN)_6\right] \xrightleftharpoons{aq} 4K^+\left[Fe(CN)_6\right]^{4-}$$

$$\underset{\substack{\uparrow\\ \text{Counter ion}}}{K_4}\left[\underset{\substack{\uparrow\\ \text{Coordinate sphere(entity)}}}{\overset{\substack{\text{Central metal atom}\\ \downarrow}}{Fe}}\left(\overset{\substack{\text{Ligand}\\ \uparrow}}{CN}\right)_6\right]\leftarrow \text{Coordination number}$$

- Coordination sphere may be anionic, cationic and neutral as well.
- Central Atom–The element that generally show coordinate covalent interaction with the is ligand is central atom, it may be metal or non –metal also. But generally in stable complexes and in widely studied complexes these central atom are **transition metals.**
- Transition Metal – The element with partially filled d –subshell (n-1) dare termed as d block element or transition element.
- Why these are called transition metal –Because transitory phase from ionic to covalent generally take place through d block (Transitory phase), so considered as transition metal

S block	**d –block**	**p-block**
Ionic	Coordinate Covalent	Covalent
Metallic	Transition Metal	Non-Metal

- Feature of d-block element – i) Metallic Character – Except Hg (Generally liquid or soft) transition metal are hard and brittle indicate covalent character of bond.
- Because of unfilled orbital of d show good conductivity
- Melting and boiling point – show high melting and boiling point, because of strong metallic bond.
- Atomic and ionic radii – within a given series ionic and atomic radii decreases with increase in atomic number (due to increase in effective nuclear charge)
- Ionization potential transition metal has high ionisation energy, they are less electropositive than s block element and do not form ionic bond
- Complex formation – Cation of transition metal has greater tendency to form complex with several molecule or ion generally because of two factors

Group	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
3- d series or 1st transition series	**Sc (21)** $3d^1 4s^2$	**Ti (22)** $3d^2 4s^2$	**V (23)** $3d^3 4s^2$	**Cr (24)** $3d^5 4s^1$	**Mn(25)** $3d^5 4s^2$	**Fe (26)** $3d^6 4s^2$	**Co(27)** $3d^7 4s^2$	**Ni (28)** $3d^8 4s^2$	**Cu(29)** $3d^{10} 4s^1$	**Zn (30)** $3d^{10} 4s^2$
4- d series or 2nd transition series	**Y(39)** $4d^1 5s^2$	**Zr (40)** $4d^2 5s^2$	**Nb (41)** $4d^2 5s^2$	**Mo (42)** $4d^5 5s^1$	**Tc (43)** $4d^5 5s^2$	**Ru (44)** $4d^7 5s^1$	**Rh (45)** $4d^8 5s^1$	**Pd (46)** $4d^{10} 5s^1$	**Ag (47)** $4d^{10} 5s^1$	**Cd (48)** $4d^{10} 5s^2$
5 - d series or 4th transition series	**Ac (89)** $6d^1 7s^2$	**Rf (104)** $5f^{14} 6s^2 7s^2$	**Db (105)** $6d^3 7s^2$	**Sg (106)** $6d^4 7s^2$	**Bb (107)** $6d^5 7s^2$	**Hs (108)** $6d^6 7s^2$	**Mt (109)** $6d^7 7s^2$	**Ds (110)**	**Ag (111)**	

- cation are relatively small in size have high Zeff.
- It has vacant inner d orbital
- The difference between (n-1)d and ns is small and it is also helpful in forming the complex corresponding to transition element .
- Striking feature of transition metal compound is their colour, rarely found in main group coordination compound.
- Coordination complex are associated with low oxidation state, (zero and negative also)
- open or incompletely field dn configuration of transition metal ion may be the presence of one or more unpaired electron, compound is also considered as radical and detected by technique such as ESR.
- The long-term stability of coordination compound with unpaired electron is the characteristic feature of coordination compound.

Exercise Questions - I

1. $K_2\left[Fe\left(CN\right)_6\right]$ is an

(A) Double salt (B) Complex salt (C) Acid (D) Base

3.1. CLASSIFICATION OF LIGANDS:

There are several ways to classify ligands and these are discussed as follows:

(i) Based upon charges

a. Neutral Ligands: H_2O, NO, CO, C_6H_6 ,*etc.*,

b. Positive Ligands: NO and $NH_2^{-}NH_3$

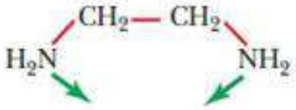
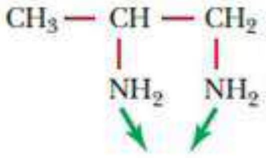
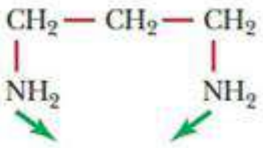
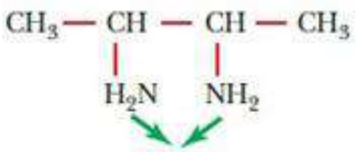
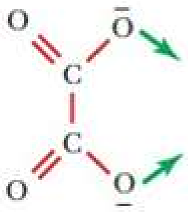
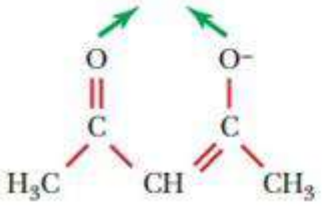
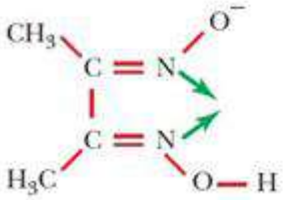
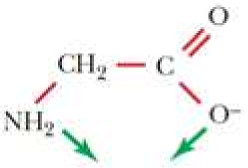
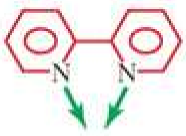
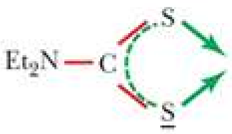
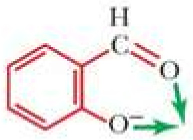
c. Negative Ligands: $Cl^{-}, NO_2, CN^{-}, OH^{-}$

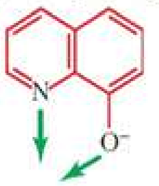
(ii) Based upon denticity of the ligand

- The number of donations accepted by a central atom from a particular ligand is known as the denticity of the ligand.
- Ligands may be classified as follows based on their denticity.

a. Monodentate: only one donation is accepted from ligand. For example, H_2O, NON CO_3^{2-}, Cl, etc.,

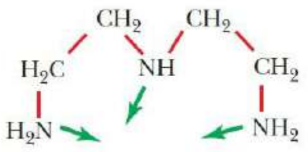
b. Bidentate: Two donations are accepted from the ligand. For example,

(i) en: ethylenediamine 	(ii) pn: propylenediamine 
(iii) tn: trimethylenediamine 	(iv) bn: butylenediamine 
(v) ox^{2-}: oxalate 	(vi) $acac^{-}$: acetylacetonate 
(vii) dmg^{-}: dimethylglyoximate 	(viii) gly^{-}: glycinate 
(ix) dipy: dipyridyl 	(x) *o*-phen: *ortho*- phenanthroline 
(xi) N, N′- Diethylthiocarbamate ion 	(xii) Salicylaldehyde anion 

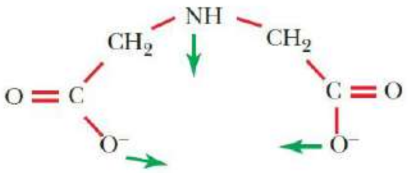
(xiii) 8-Hydroxyquinolinol ion (oxine)  	(xiv) o-Phenylenebisdimethylarsine (diarsine) 

c. Tridentate: Three donations are accepted from the ligand. For example,

(i) dien: diethylenetriamine

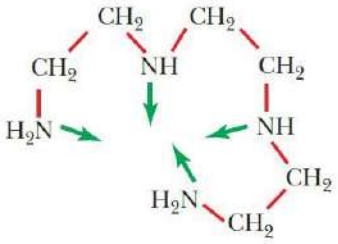


(ii) imda^{2-}: iminodiacetate

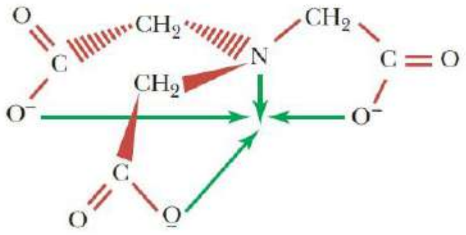


d. Tetradentate: Four donations are accepted from the ligand. For example,

(i) trien: triethylenetetraamine

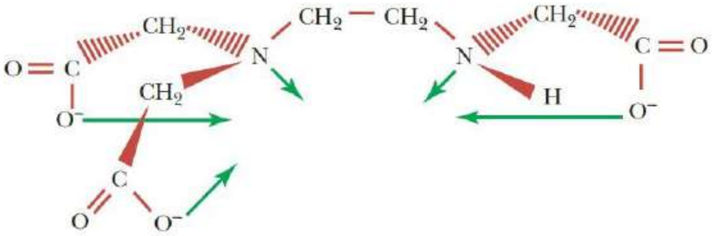


(ii) NTA^{3-}: nitrilotriacetate



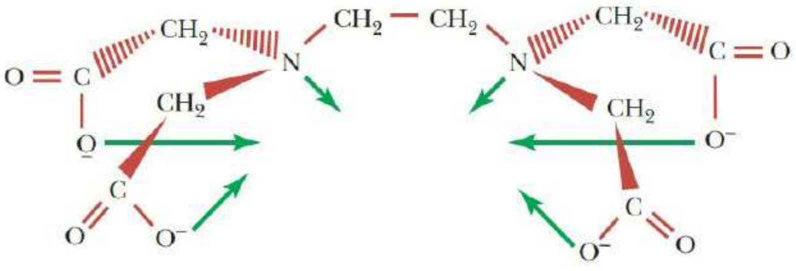
e. Pentadenate: Five donations are accepted from the ligand. For example

EDTA^{3-}: ethylenediamine triacetate



f. Hexadentate: Six donations are accepted from the ligand. For example

EDTA^{4-}: ethylenediamine tetracetate



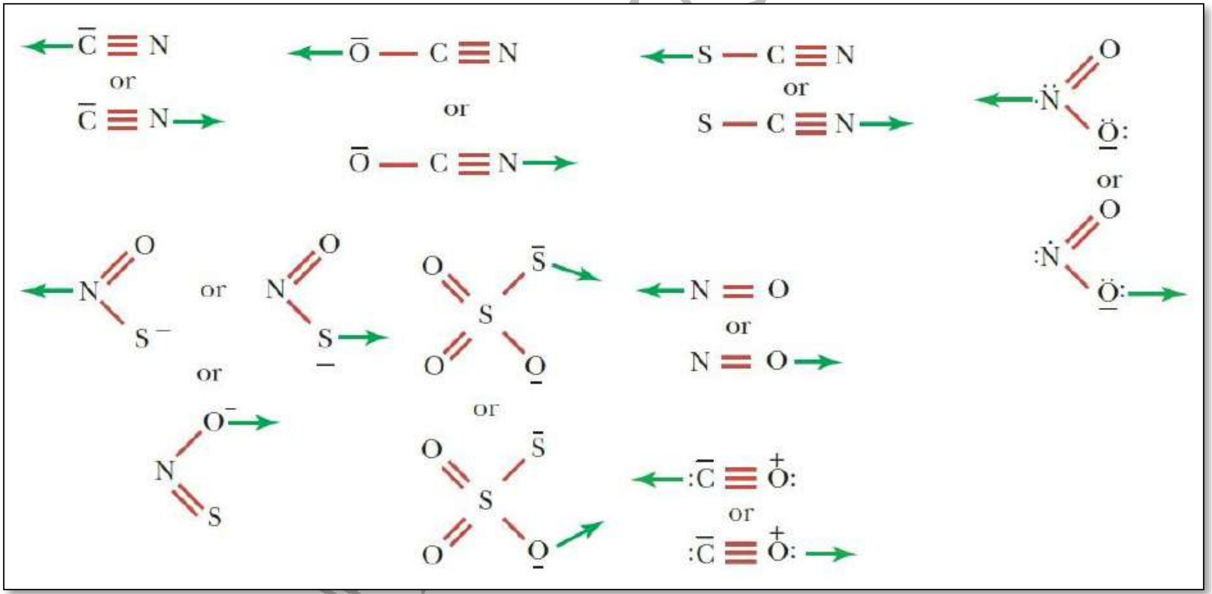
(iii) Chelating ligand:

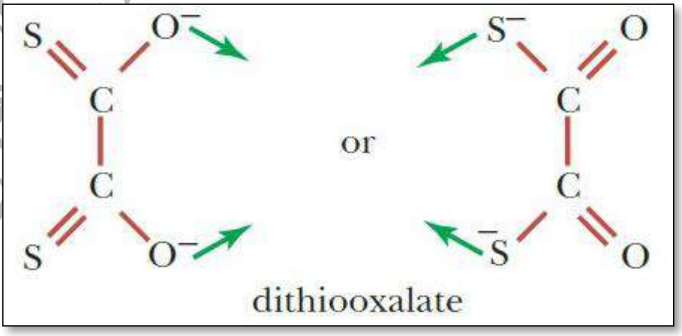
- A ligand that can form a ring structure with the central atom is called a chelating ligand. All polydentate ligands are the example of chelating ligands.
- Chelated complexes are more stable than similar complexes with monodentate ligands as dissociation of the complex involves breaking two bonds rather than one.
- However, it must be noted that NH_2NH_2 and $N-(CH_2-CH_2-)_3N$ cannot act as chelating ligands due to the formation of three membered ring and locked structure, respectively.

(iv) Ambidentate Ligand:

- A ligand that may have more than one kind of donor sites but at a time only one kind of donor site is utilized for donation is called as ambidentate ligand.
- Ambidentate ligand may be of two types.

Monodentate and Ambidentate:





Bidentate and Ambidentate

Exercise Question – II:

1. Which of the following is not a neutral ligand?

A) H_2O B) NH_3 C) ONO D) CO_2

2\. Some salts although containing two different metallic elements give test for only one of them in solution. Such salts are

A) complex B) double salts C) normal salts D) None of these

3\. An example of ambidentate ligand is

A) Ammine B) Aquo C) Chloro D) Thiocyanato

4\. Which of the following does not form a chelate?

A) EDTA B) Oxalate C) Pyridine D) Ethylenediamine

5\. A bidenate ligand always

A) has bonds formed to two metals ions

B) has a charge of +2 or – 2

C) forms complex ions with a charge of +2 or –2

D) has two donor atoms forming simultaneously two sigma (σ) bonds.

6\. An ambident ligand is one which

A) is linked to the metal atom through two donor atoms

B) has two donor atoms, but only one of them has the capacity to form a coordinate bond [or a sigma (σ)bond]

C) has two donor atoms, but either of two can form a coordinate bond

D)forms chelate rings

7\. Which of the following species is not expected to be a ligand?

A) NO B) NH_4^+

C) $NH_2CH_2CH_2NH_2$ D) Both (A) and (B)

8\. O_2 is a

A) Monodentate ligand B) Bidenate ligand

C) Tridentate ligand D) Hexadenate ligand

9. Which ligand is expected to be bidentate?

A) $C_2O_4^{2-}$ B) $CH_3 \equiv CN$ C) Br^- D) CH_3NH_2

10. Which one does not belong to ligand?

A) PH_3 B) NO^+ C) BF_3 D) Cl^-

11. $NH_2 - NH_2$ serves as

A) Monodentate ligand B) Chelating ligand

C) Bridging ligand D) Both (A) and (C)

12. Which one of the following is NOT a ligand?

A) PH_3 B) NO^+ C) Na^+ D) F^-

3.1.1. NOMENCLATURE

- Nomenclature is important in Coordination Chemistry because of the need to have an unambiguous method of describing formulas and writing systematic names, particularly when dealing with isomers.
- The formulas and names adopted for coordination entities are based on the recommendations of the International Union of Pure and Applied Chemistry (IUPAC).
- According to the Lewis base theory, the ligands are Lewis bases since they can donate electrons to the central metal atom.
- The metals, in turn, are Lewis acids since they accept electrons. Coordination complexes consist of a ligand and a metal center cation.
- The overall charge can be positive, negative or neutral. Coordination compounds are complex or contain complex ions,

(i) The central atom is listed first.

(ii) The ligands are then listed in alphabetical order. The placement of a ligand in the list does not depend on its charge.

(iii) Polydentate ligands are also listed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.

(iv) The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.

(v) There should be no space between the ligands and the metal within a coordination sphere.

(vi) When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, $\left[Co\left(CN\right)_6\right]^{3-}$, $\left[Cr\left(H_2O\right)_6\right]^{3+}$, etc.

(vii) The charge of the cation(s) is balanced by the charge of the anion(s).

- The names of coordination compounds are derived by following the principles of additive nomenclature. Thus, the groups that surround the central atom must be identified in the name.
- They are listed as prefixes to the name of the central atom along with any appropriate multipliers.

The following rules are used when naming coordination compounds:

(i) The cation is named first in both positively and negatively charged coordination entities.

(ii) The ligands are named in an alphabetical order before the name of the central atom/ion. (This procedure is reversed from writing formula).

(iii) Names of the anionic ligands end in –o, those of neutral and cationic ligands are the same except aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO. While writing the formula of coordination entity, these are enclosed in brackets ( ).

(iv) Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, *bis*, *tris*, *tetrakis* are used, the ligand to which they refer being placed in parentheses. For example, $[NiCl_2(PPh_3)_2]$ is named as dichloridobis (triphenylphosphine) nickel (II).

(v) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.

(vi) If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix – ate.

- For example, Co in a complex anion, $\left[Co(SCN)_4\right]^{2-}$ is called cobaltate. For some metals, the Latinnames are used in the complex anions, *e*.g., ferrate for Fe.The neutral complex molecule is named similar to that of the complex cation.

The following examples illustrate the nomenclature for co ordination compounds.

1. $\left[Cr(NH_3)_3(H_2O)_3\right]Cl_3$ **is named as: triamminetria quachromium (III) chloride**

Explanation**:** The complex ion is inside the square bracket, which isa cation. The amine ligands are named before the aqua ligands according to alphabetical order. Since there are three chloride ions in the compound, the charge on the complex ion must be +3 (since the compound is electrically neutral). From the charge on the complexion and the charge on the ligands, we can calculate the oxidation number of the metal. In this example, all the ligands are neutral molecules. Therefore, the oxidation number of chromium must be the same as the charge of the complex ion, +3.

2. $\left[Co(H_2NCH_2CH_2NH_2)_3\right]_2(SO_4)_3$ **is named as:tris(ethane-1,2–diamine)cobalt(III) sulphate**

Explanation**:** The sulphate is the counter anion in this molecule. Since it takes 3 sulphates to bond with two complex cations, the charge on each complex cation must be +3. Further, ethane-1,2–diamine is a neutral molecule, so the oxidation number of cobaltin the complex ion must be +3. *Remember that you never have to indicate the number of cations and anions in the name of anionic compound.*

3. **Consider the example** $[Pt(NH_3)_4][PtCl_4]$.

Solution: In this case one coordination sphere is positive and the other is negative. Pt shows two variable stable oxidation states +2 and +4. Positive and negative charges on positive and negative coordination spheres hould satisfy one of the oxidation states.

If we consider one negative charge on the right side coordination sphere, then charge on the cation should be +1. Thus, oxidation state of Pt in complex cation and complex anion is calculated as

Complex Cation	**Complex Anion**
$\left[Pt(NH_3)_4\right]^+$	$\left[PtCl_4\right]^-$
$x+0=+1$	$x-4=-1$
$x=+1$	$x=+3$

- Thus, oxidation states of Pt is+1 and+3 which are not the stable oxidation states of Pt. Thus, this is wrong
- If we consider the -2 charge on the anion, then +2 charge will be on cation. Thus, oxidation state of Pt can be calculated as

Complex Cation	**Complex Anion**
$\left[Pt(NH_3)_4\right]^{2+}$	$\left[PtCl_4\right]^{2-}$
$x+0=+2$	$x-4=-2$
$x=+2$	$x=+2$

Thus, oxidation state of P tin both the complexion is+2 (correct).

4.$\left[Ag(NH_3)_2\right]\left[Ag(CN)_2\right]$**: diamminesilver (I) dicyanidoargentate (I)**

5. $\left[Co(NH_3)_3Cl_3\right]$**: Triamminetrichlorocobalt (III)**

Exercise Questions:

1. $\left[Co(NH_3)_3(NO_2)_3\right]$
2. $\left[Co(NH_3)_6\right]Cl_3$
3. $\left[Co(en)_3\right]Cl_3$
4. $Co(en)_3]\left[Cr(CN)_6\right]$
5. $[Pt(py)4][PtCl4]$
6. $[Pt(NH_3)_4Cl_2[PtCl_4]$
7. $\left[Co(NH_3)_6\right]\left[Cr(NH_3)_2Cl_4\right]_3$
8. $\left[Fe(NH_3)_6\right]\left[Fe(CN)_6\right]$
9. $\left[Cr(en_3)_6\right]Cl_3$
10. $\left[CuCl(CH_3NH_2)_2\right]$
11. $Fe(C_5H_5)_2$

12. $\left[Ni\left(CO\right)\right]_4$

13. $\left[Fe\left(C_5H_5\right)_2\right]$

14. $\left[Ni\left(PF_3\right)_4\right]$

15. $\left[CuCl_2\left\{O=C\left(NH_2\right)_2\right\}_2\right]$

16. $\left[R\left(NCS\right)_3\left(NH_3\right)_3\right]$

17. $\left[Pdl_2\left(ONO\right)_2\left(H_2O\right)_2\right]$

18. $\left[Ni\left(NH_3\right)_2\left(en\right)\right]\left(CH_3COO\right)_2$

19. $\left[Co\left(NH_3\right)_4\left(H_2O\right)Cl\right]Cl_2$

20. $\left[Co\left(NH_3\right)_4SO_4\right]NO_3$

21. $\left[Co\left(NH_2\right)_2\left(NH_3\right)_4\right]Br$

22. $\left[Cr\left(H_2O\right)_4Cl_2\right]NO_3$

23. $\left[CO\left(NH_3\right)_6\right]Cl_3$

24. $Li[AlH_4]$

25. $K_4\left[Fe\left(CN\right)_6\right]$

26. $Na\left[PtBrCl\left(ONO\right)\left(NH\right)_3\right]$

27. $K_2\left[Co\left(N_3\right)_4\right]$

28. $K_2\left[Cu\left(CN\right)_4\right]$

29. $K_4\left[Ni\left(CN\right)_4\right]$

30. $K_4\left[Ni\left(CN\right)_2\left(C_2O_4\right)_2\right]$

31. $Na_2[OsCl_5N]$

32. $K_4[Mn\left(NCS\right)_6].3H_2O$

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UNIT-4
GASEOUS STATE & SOLID STATE

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INDEX - UNIT 4

UG TRB – CHEMISTRY – 2023-24

PHYSICAL CHEMISTRY - UNIT 4

GASEOUS STATE & SOLID STATE

4.1. GASEOUS STATE

4.1.1. Gas laws:

- All matters exist in three states gas, liquid and solid.
  - A **Solids** have a definite shape and definite volume. This is because in solids the ions are closely packed in certain order in fixed positions in the crystal lattice, the particle in a solid are not free to move about but vibrate in their fixed position, so the intermolecular force of attraction is greater.
  - A **Liquids** have no definite shape but have definite volume. In liquids, the intermolecular force of attraction is smaller than that in solids. So the particles do not have a fixed position.
  - A **Gases** have no definite shape and volume. Here the particles are far apart and hence they have no force of attraction. A gas consist of molecules separated wide apart in empty space, the molecules are free to move about throughout the container.

Comparison between the Three States of Matter:

Properties	Solid State	Liquid State	Gaseous State
Shape an volume	**Have definite shape and volume**	**No definite shape but have definite volume**	**Have no definite shape and volume**
Inter molecular force of attraction	**Strong**	**In between solids and gases**	**Very small**
Arrangement of particles	**Closely packed**	**Loosely packed**	**Far apart**
K.E of particles	**Very low**	**In between solids and gases**	**Very high**
Diffusability	**Very low**	**In between solids and gases**	**Very high**
Compressibility	**Very low**	**In between solids and gases**	**Very high**

General characteristics of Gases:

- Gas has limitless expansibility. They expand to fill the entire vessel they are placed in
- Gases are easily compressed by application of pressure to a movable piston fitted in the container.
- Gases can diffuse rapidly through each other to form a homogeneous mixture.
- Gases exert pressure on the walls of the containers in all directions.
- When a gas confined in a vessel is heated, its pressure increased. Upon heating in a vessel fitted with a piston, volume of the gas increases.
- Pressure. Gases exert pressure on the walls of the container in all direction. You can site the example of a gas balloon.

Parameters of a Gas:

- A gas sample can be described in terms of four parameters
- the volume, V of the gas
- it's pressure, **P**

- it's temperature, **T**
- the number of moles, n, of gas in the container

Volume:

- The volume of the container is the volume of the gas sample. It's is usually given in litre or millilitres
  - 1 litre (l) = 1000ml and $1\ ml = 10^{-3} l$

Pressure:

- The pressure of a gas is defined as the force exerted by the impact of its molecules per unit surface area in contact.
- The pressure of a gas sample can be measured with the help of a **mercury manometer**.
- The atmospheric pressure can be determined with a **mercury barometer**.
  - 1 atm = 760 mm Hg = 760 torr $= 1.013 \times 10^5 Pa$.

Temperature:

- The temperature of a gas may be measured in centigrade degrees $\left(^\circ C\right)$ or celsius degrees. The SI unit of temperature is Kelvin (K)
  - $K = ^\circ C + 273$

The Moles of a Gas Sample, n:

- The number of moles, n, of a sample of a gas in a container can be found the mass, m of the sample by dividing the molar mass, M
  - Moles of a gas (n) = mass of gas sample (m)/ molecular mass of gas(M)

Measurable Properties of Gases:

- **Mass:** The mass of gas is generally used in the form of number of moles which is related as

(i) $no.of\ moles = \dfrac{wt.in.gm}{Molecular\ mass\ of\ gases}\left(n = \dfrac{w}{M}\right)$

(ii) $number\ of\ moles = \dfrac{no.\ of\ molecules\ of\ given\ gas}{Avogadro's\ number\ of\ molecules}\left(n = \dfrac{N}{N_A}\right)$

(iii) $no.\ of\ moles = \frac{volume\ of\ given\ gas\ in\ litters\ at\ STP}{22.4L}$

Volume :

- Volume of gas is volume of the container in which it is present, i.e space which the gas molecules can occupy.

Relation Between Different Units of Volume :

- $1m^3 = 10^3 dm^3 = 10^3 litre = 10^6 cm^3 = 10^6 ml = 10^9 mm^3$

Temperature:

Degree of Hotness or Coldness of a Body is Measured by Temperature:

- $\frac{C}{100} = \frac{K-273}{100} = \frac{F-32}{180}$
- **C-Celsius scale , K – Kelvin scale, F- Fahrenheit scale**

Note:

- In all the problem of gaseous state (i.e . in all gas law equations), temperature must be expressed in Kelvin scale i.e.. $t^\circ C + 273.15 = TK$

Pressure:

- Pressure of gas is defined as the force excreted by the on the walls of it's container It is often assumed that pressure is isotropic, i.e it is the same in all the three directions.

4.1.2. The Gas Laws:

- These are some relationships connecting the measurable properties of gases like pressure (P), temperature (T), volume (V) and number of moles (n). These are some relationships connecting the measurable properties of gases like pressure (P), temperature (T), volume (V) and number of moles (n).

Postulates of Kinetic Theory of Gases:

1. Every gas consists of large number of tiny particles called point masses i.e. the actual volume of molecules is negligible when compared to the total volume of the gas. For the same gas, all molecules are of same size and mass.

2. The gas molecules are always in a state of rapid zig-zag motion in all directions. These molecules collide with each other and with the walls of the containing vessel.

3. A molecule moves in a straight line with uniform velocity between two collisions.

4. The molecular collisions are perfectly elastic so that there is no net loss of energy when the gas molecules collide with one another or against the walls of the vessel. Suppose two molecules collide having same mass m. Before collision the velocity of one molecule is υ_1 and velocity of other molecule is υ_2 and after collision the velocity of the molecule's changes from υ1to υ_1' and from υ_2 to υ_2' then if the collisions are elastic there is no loss of kinetic energy. This can be expressed as follows.

Total kinetic energy of two molecules before collision is

$$\frac{1}{2}m_1\upsilon_1{}^2 + \frac{1}{2}m_2\upsilon_2{}^2$$

And after collision total kinetic energy of both the molecules is

$$\frac{1}{2}m_1\upsilon_1{}^{'2} + \frac{1}{2}m_2\upsilon_2{}^{'2}$$

If $\frac{1}{2}m_1\upsilon_1{}^2 + \frac{1}{2}m_2\upsilon_2{}^2 = \frac{1}{2}m_1\upsilon_1{}^{'2} + \frac{1}{2}m_2\upsilon_2{}^{'2}$

i.e. total kinetic energy before collision is equal to total kinetic energy after collision then the collision is said to be an elastic collision.

5. There are no attractive forces operating between molecules or between molecules and the walls of the vessel in which the gas has been contained. The molecule move independently of one another.

6. The pressure of the gas is the hits recorded by the molecules on the walls of the container in which the gas is contained.

7. The average kinetic energy of gas molecules is directly proportional to absolute temperature. This means that the average kinetic energy of molecules is the same at a given temperature. This must be clear to you that all the above postulates are applicable to ideal gases only i.e. the gas which obey Boyle's and Charle's law under all conditions of temperature and pressure. These are only approximately valid for real gases.

Derivation of Kinetic Gas Equation:

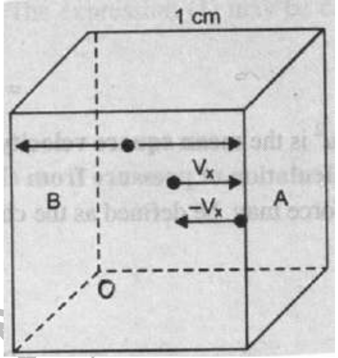
- Suppose a volume of gas enclosed in a cubical vessel at a fixed temperature
- Suppose that:
  - The length of each side of cube = *l* cm

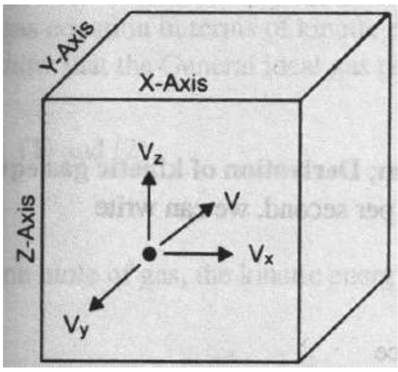
- the number of gas molecules = n
- the mass of one molecule = m
- the velocity of a molecule = υ

- Let us consider one single molecule of a gas can be evaluated by calculating the momentum during collisions.
- According to kinetic model the molecules of the gas are moving in straight lines in all possible directions.
- They collide with one another frequently as also with the walls of the container. Since their mutual collisions are perfectly elastic and do not involve the loss of energy, these may be neglected. Here we will, therefore, assume that gas molecules move in all directions but rebound whenever they strike the wall of the container. Now you proceed to derive kinetic gas equation in the following steps According to the kinetic theory, a molecule of a gas can move with velocity in any direction velocity is a vector quantity can be resolved into components *x, y, z* along the X, Y and Z axes. These components are related to velocity υ by the following expression.

$$\upsilon^2 = \upsilon_x{}^2 + \upsilon_y{}^2 + \upsilon_z{}^2$$

- Let us consider a molecule moving in OX direction between opposite faces A and B. It will strike the face A with velocity *x* and rebound with velocity - *x*. To hit the same face again the molecule must travel *l* cm to Collide with opposite face B and then again *l* cm to return to face A. Therefore, time taken between two collisions can be calculated as follows:





- The molecule travels υ_x cm in 1 sec

hence1 cm in $1/\upsilon_x$ sec

And 2*l* cm in $2l/\upsilon_x$ sec

In $2l/\upsilon_x$ sec molecule suffers 1 collision

In 1 sec no of collisions = $\upsilon_x/2l$

Each impact of the molecule on the face A causes a change of momentum which is mass X velocity.

Momentum of the molecule before impact $= m\upsilon_x$

Momentum of the molecule after impact $= -m\upsilon_x$

Hence change of momentum $= m\upsilon x - (-m\upsilon x) = 2m\upsilon x$

But the number of collisions per second on face $A = \upsilon x / 2l$

- Therefore, total change of momentum per second on face A caused by one Molecule

$$= 2m\upsilon x^2 / 2l$$

$$= m\ \upsilon x^2 / l$$

- As there are two faces along x- direction, total change of momentum per second
- Considering both the faces along x-direction will be $2m\upsilon x^2 / l$
- This is change of momentum caused by one molecule along x-direction per second will be $2m\ \upsilon z^2 / l$. The change of momentum caused by one molecule along y- direction per second will be $2m\ \upsilon y^2 / l$ and change of momentum caused by one molecule along z- direction per second will be
- Total change of momentum caused by one molecule considering along three direction will be

$$= 2m\ \upsilon x^2 / l + 2m\ \upsilon y^2 / l + 2m\ \upsilon z^2 / l$$

$$= 2m / l\ \left(\upsilon x^2 + \upsilon y^2 + \upsilon z^2\right)$$

$$= 2m\ \upsilon^2 / l$$

- Since there are n molecules in the vessel then total change of momentum due to n molecules will be $2mn\ \upsilon^2 / l$

$\upsilon^2 =$ mean square velocity

- Since change of momentum per second is force

Hence force $= 2mn\upsilon^2 / l$

Since pressure = Total force/Total area

- Since there are six faces in a cube, area of each cube is l^2. Hence total area is $6l^2$.
- Then pressure $= 2mn\upsilon^2 / lx\ 1/6l^2 = mn\upsilon^2 / 3l^2$

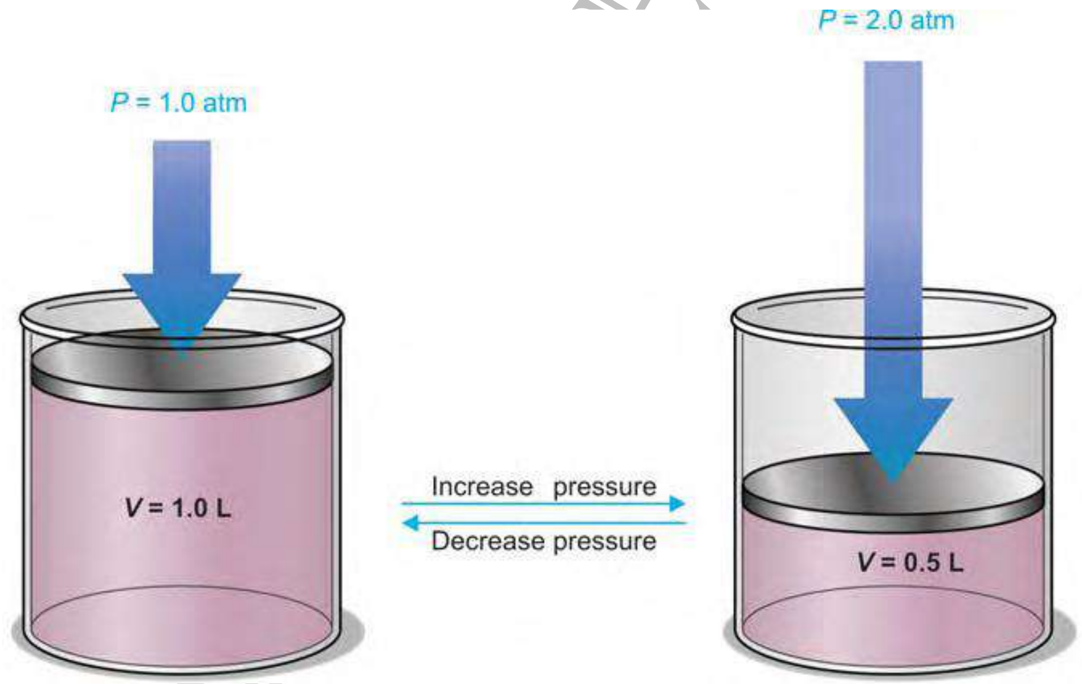
As l^2 = volume V

Hence pressure $P = 1/3\, mn\upsilon^2 / V$

(or) $\mathbf{PV = 1/3\ mn\upsilon^2}$

- This is known as **Kinetic Gas Equation**. This equation has been derived for a cubical vessel. It is equally valid for vessel of any shape. The available volume in the vessel may be considered as made up of large number of infinitesimally small cubes, for each of them the equation is valid.

Boyle's Law (Pressure -Volume Relationship):



- It states that at constant temperature, the volume of a fixed mass of gas is inversely proportional to its pressure.
- The Boyle law may be express mathematically,

$V \alpha 1/P$

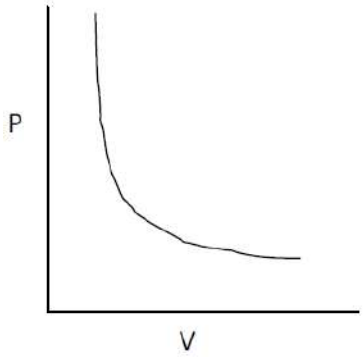
$V = k\, x\, 1/P,$

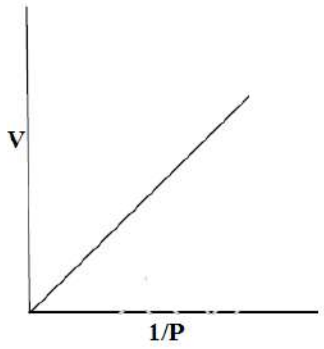
- where *k* is the proportionality constant.

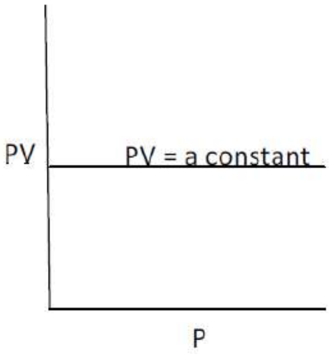
(or) PV = k, a constant

- Consider a fixed amount of gas at constant temperature T. Let V_1 & P_1 are its initial volume and pressure respectively. Let the gas undergoes expansion, so that its final volume and pressure becomes V_2 and P_2.
- Then according to Boyle's law,

  $P_1V_1 = k = P_2V_2$; $P_1V_1 = P_2V_2$
- If we plot graphs between pressure against volume (hyperbola), volume against 1/pressure (straight line) and PV against P at constant temperature, the graphs obtained are as follows
- These graphs are obtained at constant temperature and are called **isotherms**







Consequence of Boyle,s Law:

- The pressure-density relationship can be derived fromthe boyle,s law as

  $P_1V_1 = P_2V_2$ (Boyle,s law)

  $P_1(m/d_1) = P_2(m/d_2)$

  $\mathbf{P_1 / d_1 = P_2 / d_2}$

1. A gas is present at a pressure of 2atm. What should be the increase in pressure so that the volume of the gas can be decreased to ¼ th of the initial value if the initial value if the temperature is maintained constant.

Sol : PV = constant for a given mass of gas at constant pressure

$\Rightarrow P_1V_1 = P_2V_2 \quad P_1 = 2atm \quad V_1 = V \quad V_2 = V/4 \quad P_2 = ?$

Now, $2\times V = P_2 = \frac{V}{4} \Rightarrow P_2 = 8atm$ increase

Pressure should be increased from 2 to 8 atm.

Total increase $= 8 - 2 = 6\ atm$

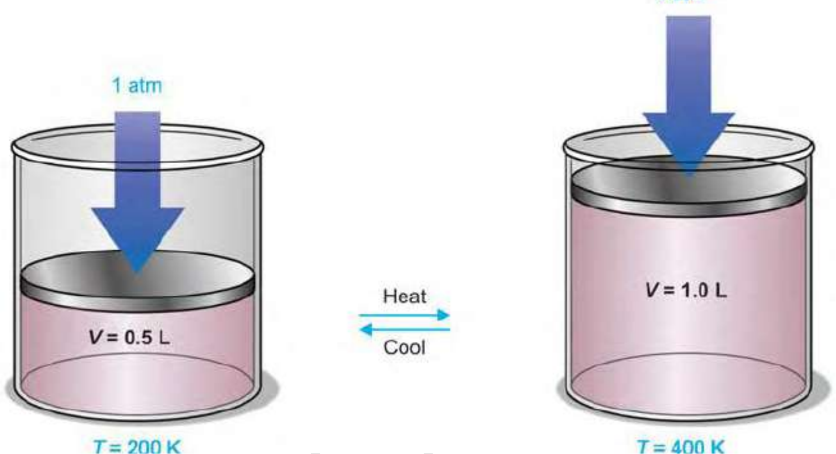
A sample of gas occupies 10 litre under a pressure of 1 atmosphere. What will be its volume if the pressure is increased to 2 atmospheres? Assume that the temperature of the gas sample does not change .

Ans: 5 Litre

4.1.3. Charles' Law (Temperature -Volume Relationship)

- It states that at constant pressure, volume of a fixed mass of gas is directly proportional to its temperature. Mathematically, $V \alpha\ T$

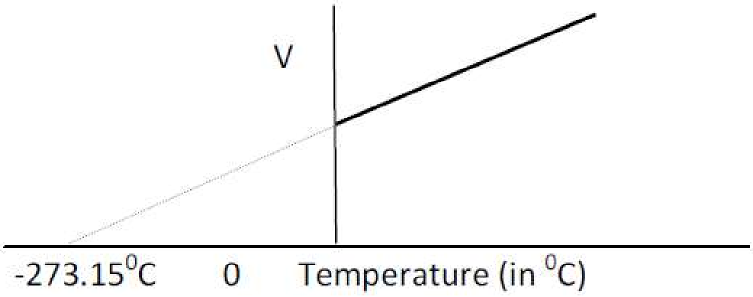
$V = k\ x\ T; V / T = k,$ a constant



- Consider a fixed amount of gas at constant pressure P. Let V_1 be its volume at a temperature T_1 and V_2 be its volume at a temperature T_2.

Then according to Charle's Law:

- $V_1 / T_1 = V_2 / T_{2;}$ Since the graph is obtained at constant pressure, it is called **isobar**
- If volume is plotted against temperature at constant pressure, the graph obtained is as follows



Since the graph is obtained at constant pressure, it is called **isobar**

A gas occupies a volume of 580 ml at $17^{\circ}C$. It is heated to $100^{\circ}C$ at constant pressure. Calculate the volume of the gas

(A) 746 ml **(B) 760ml** **(C) 773ml** **(D) 780ml**

Ans . A

Sol :

Initial volume $(V_1) = 580ml,$

$$T_1 = 17 + 273 = 290K$$

Find the volume $(V_2) = ?$

$$T_2 = 100 = 273 = 373K$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\therefore V_2 = T_2 \times \frac{V_1}{T_1} = 373 \times \frac{580}{290} = 746ml$$

A gas occupies 3 litters at and one atmospheric . hat volume will it occupy if the temperature is changed , the pressure remaining constant-

(A) 2.91 litres **(B) 2.86 litres** **(C) 2.30 litres** **(D) none of these**

Ans : (b) 2.86 litres

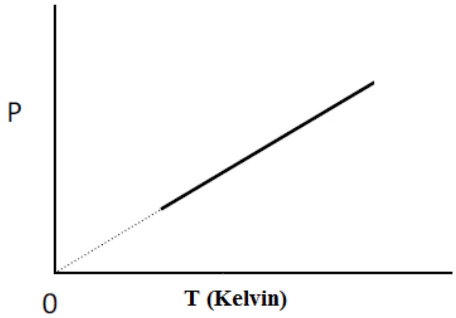
4.1.4. Gay Lussac's Law (Pressure-Temperature Relationship):

- It states that at constant volume, the pressure of a fixed amount of a gas is directly proportional to the kelvin temperature.
- Mathematically,

$$P \alpha T$$

(or) P = a constant $\times T$

(or), P/T = a constant



- If we plot a graph between pressure and temperature of a fixed mass of gas at constant volume, the graph obtained is as follows.
- The above is obtained at constant volume and is termed as an **isochore.**

4.1.5. Avogadro Law (Volume-no. of Moles or Amount Relationship):

- It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of moles or molecules. This means that at constant temperature and pressure, the volume of a gas is directly proportional to its number of moles (n) or molecules (N).

$V \ \alpha \ n,$2the number of moles

$V = k \times n,$ where k is a constant; $V/n = k;$ for any two gases with volumes V_1, V_2 and moles n_1, n_2 at constant T and $P. V_1/n_1 = A = V_2/n_2$

$V_1 = V_2; \ n_1 = n_2$

- We know that number of moles (n) = mass in gram (m)/molar mass (M)

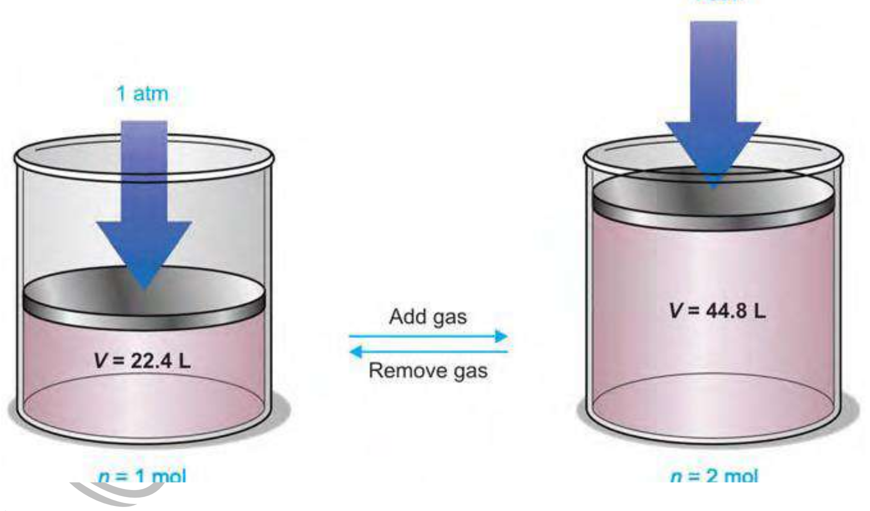
  i.e., n = m/M

- So, the above equation becomes:

  $V = k \ x \ m/M$

  Or, $M = k \ x \ m/V; \ M = k \ x \ d; M \ \alpha \ d$

- The density of a gas is directly proportional to its molar mass.



Molar Gas Volume:

- The molar gas volume its follow as a corollary of Avogadro law that one mole of any gas at a given temperature and pressure has the same fixed volume.It is called the **molar gas volume.**

  1 mole of a gas at STP = $22.7109 \ litres \ mol^{-1}$

Question for Practice:

1. Which of the following does not express the properties of gases?

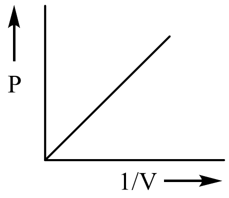
(A) Gases are highly compressible.

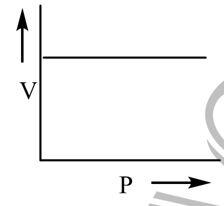
(B) Gases exert pressure equally in all directions.

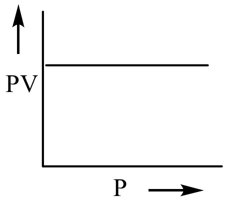
(C) Gases have much higher density than liquids and solids.

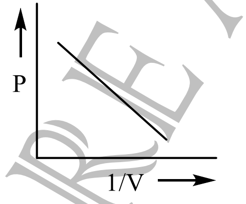
(D) Gases mix evenly and completely in all proportions.

2.Which of the following graphs represents the incorrect Boyles law (correct ansB)

a)


b)


c)


d)


3. A flask of capacity 2L is heated from $35^{o}C$ to $45^{o}C$ what volume of air will escape from the flask?

(A)10 ml (B) 24 ml (C) 65 ml (D) 50 ml

4. Absolute zero can be defined as the temperature at which

(A) pressure becomes zero (B) volume becomes zero

(C) mass becomes zero (D) density becomes zero

5. If we plot volume of a certain mass or volume of gas against temperature at constant pressure. this graph known as

(A) isochore (B) isotherm (C) isotone (D) isobar

6. Mathemtically, Boyles law can be represented as

(A) $V \alpha 1/P$ (B) $V = K/P$ (C) $VP=K$ (D) all of these

7. At constant temperature, the pressure of the gas is reduced to one third, the volume

(A) reduced the one third (B) increased by three times

(C) cannot be predicted (D) remains same

Density $= \dfrac{n \times at.wt}{V \times N_A}$

$$7.2 = \frac{3 \times at.wt}{24 \times 10^{-24} cm^3}$$

6.023×10^{23}

At.wt = 34.69

34.69 g has no.of atoms $= 6.023 \times 10^{23}$

200g has no of atoms $= \dfrac{6.023 \times 10^{23} \times 200}{34.69}$

$= 3.4722 \times 10^{24}\, atoms$

$= approx..\ 3.5 \times 10^{24}\, atoms$

4.3. Multiple Choice Questions

1. Which of the following is not a close packing

A) hcp B) ccp C) bcc D) fcc

2. Which of the following has HCP structure

A) Al B) Mg C) Cu D) Ni

3. All Nobel gases crystallise in the ccp structure except

A) Helium B) Neon C) Argon D) Krypton

4. If the coordination number of an element in its crystal lattice is 8, then packing is

A) FCC B) HCP

C) BCC D) None of the above

5. In close packed lattice the number of octahedral sites as compared to tetra ones will be

A) equal B) Half C) Double D) One fourth

6. A compound contains P and Q element, atoms Q are ccp arrangement While P occupy all tetrahedral sites. Formula of compound is

A) PQ B) PQ_2 C) P_2Q D) P_3Q

7. The co-ordintion number of Zn^{2+} and S^{2-} ions in the zinc blende (ZnS) type structure is______________

A) 4:4 B) 6:6 C) 8:8 D) 4:8

8. Antifluorite structure is derived from fluorite structure by

A) Heating fluorite crystal lattice

B) Subjecting fluorite structure to high pressure

C) Interchanging the position of positive and negative ions in the lattice

D) All the above

9. At zero Kelvin, most of the ionic crystal posses

A) Frenkel defect B) Schottky defect

C) Metal excess defect D) No defect

10. As a result of schottky defect

A) there is no effect on the density B) density of the crystal increase

C) density of the crystal decreases D) any of the above three can happen

11. Frenkel defect is generally observed in

A) AgBr B) AgI

C) ZnS D) All of these

12. F-centres in an ionic crystal are

A) lattice sites containing electron B) interstitial sites continuing electron

C) lattice sites that are vacant D) interstitial sites containing cations

13. The correct statement regarding F-centre is

A) Electrons are held in the lattice sites of crystal

B) F-centre imparts colour to the crystal

C) Conductivity of the crystal increases due to F-centre

D) All the three above

14. For tetragonal crystal system which of the following is not true

A) $a = b \neq c$ B) $\alpha = \beta = \gamma = 90^o$

C) $a \neq b \neq c$ D) $\alpha = \beta \neq \gamma = 90^o$

15. In an ionic crystal, a cation and an anion leave the lattice to cause two vacancies. This defect is called

A) Schottky defect	B) Frenkel defect
C) interstitial defect	D) none of these

16. Which of the following defects is generally found in sodium chloride and cesium chloride?

A) Frenkel defect	B) interstitial defect
C) Schottky defect	D) none of these

17. In a solid lattice, a cation has left a lattice site and is present in interstitial position, the lattice defect is

A) Schottky defect	B) Frenkel defect
C) vacancy defect	D) interstitial defect

18. In Frenkel defect,

A) some of the lattice sites are vacant

B) an ion occupies interstitial position

C) some of the cations are replaced by foreign ions

D) none of the above

19. A device used to convert light energy into electrical energy is called

A) a semiconductor	B) a solar cell
C) an irreversible cell	D) an electrochemical cell

20. For an ionic crystal of formula AX, the radius ratio lies between 0.732 and 0.414. Its co-ordination number is

A) 4	B) 6	C) 8	D) 12

21. The radius ratio in an ionic crystal lies between 0.732–1.000, the co-ordination number is

A) 3	B) 4	C) 6	D) 8

22. The number of atoms per unit cell in a simple cubic, fcc and bcc are

A) 1, 2, 4	B) 1, 4, 2	C) 4, 2, 1	D) 2, 4, 1

23. In a crystal, the atoms are located at the positions where potential energy is

A) maximum	B) zero	C) minimum	D) infinite

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UG TRB
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UNIT-5
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UG TRB – CHEMISTRY – 2023-24

INORGNIC CHEMISTRY - UNIT 5

THERMODYNAMICS

5.1. INTRODUCTION:

❖ Thermodynamics, science of the relationship between heat, work, temperature, and energy. In broad terms, thermodynamics deals with the transfer of energy from one place to another and from one form to another.

❖ The key concept is that heat is a form of energy corresponding to a definite amount of mechanical work.

❖ Heat was not formally recognized as a form of energy until about 1798, when Count Rumford (Sir Benjamin Thompson), a British military engineer, noticed that limitless amounts of heat could be generated in the boring of cannon barrels and that the amount of heat generated is proportional to the work done in turning a blunt boring tool. Rumford's observation of the proportionality between heat generated and work done lies at the foundation of thermodynamics. Another pioneer was the French military engineer Sadi Carnot, who introduced the concept of the heat-engine cycle and the principle of reversibility in 1824. Carnot's work concerned the limitations on the maximum amount of work that can be obtained from a steam engine operating with a high-temperature heat transfer as its driving force. Later that century, these ideas were developed by Rudolf Clausius, a German mathematician and physicist, into the first and second laws of thermodynamics, respectively.

❖ Thermodynamics is the study of the relations between heat, work, temperature, and energy. The laws of thermodynamics describe how the energy in a system changes and whether the system can perform useful work on its surroundings. It is represented in the Figure 1.

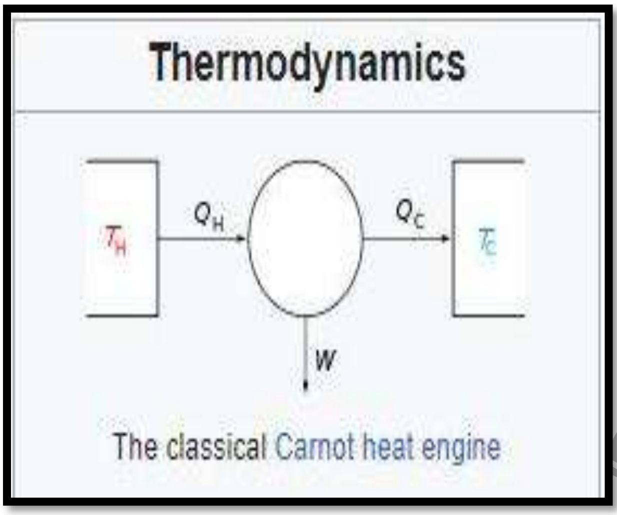


Figure 1: Representation of Flow of heat and Work

- The history of thermodynamics as a scientific discipline generally begins with Otto von Guericke who, in 1650, built and designed the world's first vacuum pump and demonstrated a vacuum using his Magdeburg hemispheres. Guericke was driven to make a vacuum in order to disprove Aristotle's long-held supposition that 'nature abhors a vacuum'. Shortly after Guericke, the Anglo-Irish physicist and chemist Robert Boyle had learned of Guericke's designs and, in 1656, in coordination with English scientist Robert Hooke, built an air pump. Using this pump, Boyle and Hooke noticed a correlation between pressure, temperature, and volume. In time, Boyle's Law was formulated, which states that pressure and volume are inversely proportional. Then, in 1679, based on these concepts, an associate of Boyle's named Denis Papin built a steam digester, which was a closed vessel with a tightly fitting lid that confined steam until a high pressure was generated.

- Later designs implemented a steam release valve that kept the machine from exploding. By watching the valve rhythmically move up and down, Papin conceived of the idea of a piston and a cylinder engine. He did not, however, follow through with his design. Nevertheless, in 1697, based on Papin's designs, engineer Thomas Savery built the first engine, followed by Thomas Newcomen in 1712. Although these early engines were crude and inefficient, they attracted the attention of the leading scientists of the time.

- The fundamental concepts of heat capacity and latent heat, which were necessary for the development of thermodynamics, were developed by Professor Joseph Black at the University of Glasgow, where James Watt was employed as an instrument maker. Black and Watt performed experiments together, but it was Watt who conceived the idea of the external condenser which resulted in a large increase in steam engine efficiency. Drawing on all the previous work led Sadi Carnot, the "father of thermodynamics", to publish Reflections on the Motive Power of Fire (1824), a discourse on heat, power, energy and engine efficiency. The book outlined the basic energetic relations between the Carnot engine, the Carnot cycle, and motive power. It marked the start of thermodynamics as a modern science.

- The first thermodynamic textbook was written in 1859 by William Rankine, originally trained as a physicist and a civil and mechanical engineering professor at the University of Glasgow. The first and second laws of thermodynamics emerged simultaneously in the 1850s, primarily out of the works of William Rankine, Rudolf Clausius, and William Thomson (Lord Kelvin). The foundations of statistical thermodynamics were set out by physicists such as James Clerk Maxwell, Ludwig Boltzmann, Max Planck, Rudolf Clausius and J. Willard Gibbs.
- Clausius, who first stated the basic ideas of the second law in his paper "On the Moving Force of Heat",published in 1850, and is called "one of the founding fathers of thermodynamics", introduced the concept of entropy in 1865.
- During the years 1873to 1876 the American mathematical physicist Josiah Willard Gibbs published a series of three papers, the most famous being “On the Equilibrium of Heterogeneous Substances”, in which he showed how thermodynamic processes, including chemical reactions, could be graphically analyzed, by studying the energy, entropy, volume, temperature and pressure of the thermodynamic system in such a manner, one can determine if a process would occur spontaneously. Also Pierre Duhem in the 19th century wrote about chemical thermodynamics.
- During the early 20th century, chemists such as Gilbert N. Lewis, Merle Randall, and Guggenheim applied the mathematical methods of Gibbs to the analysis of chemical processes.
- Thermodynamics is a branch of physics that deals with heat, work, and temperature, and their relation to energy, entropy, and the physical properties of matter and radiation.
- The behavior of these quantities is governed by the four laws of thermodynamics which convey a quantitative description using measurable macroscopic physical quantities, but may be explained in terms of microscopic constituents by statistical mechanics.

- Thermodynamics applies to a wide variety of topics in science and engineering, especially physical chemistry, biochemistry, chemical engineering and mechanical engineering, but also in other complex fields such as meteorology.
- Historically, thermodynamics developed out of a desire to increase the efficiency of early steam engines, particularly through the work of French physicist Sadi Carnot (1824) who believed that engine efficiency was the key that could help France win the Wars. Cots-Irish physicist Lord Kelvin was the first to formulate a concise definition of thermodynamics in 1854 which stated, "Thermo-dynamics is the subject of the relation of heat to forces acting between contiguous parts of bodies, and the relation of heat to electrical agency."
- German physicist and mathematician Rudolf Clausius restated Carnot's principle known as the Carnot cycle and gave so the theory of heat a truer and sounder basis. His most important paper, "On the Moving Force of Heat", published in 1850, first stated the second law of thermodynamics. In 1865 he introduced the concept of entropy. In 1870 he introduced the virial theorem, which applied to heat.
- The initial application of thermodynamics to mechanical heat engines was quickly extended to the study of chemical compounds and chemical reactions. Chemical thermodynamics studies the nature of the role of entropy in the process of chemical reactions and has provided the bulk of expansion and knowledge of the field. Other formulations of thermodynamics emerged.
- Statistical thermodynamics, (or) statistical mechanics, concerns itself with statistical predictions of the collective motion of particles from their microscopic behavior. In 1909, ConstantinCarathéodory presented a purely mathematical approach in an axiomatic formulation, a description often referred to as geometrical thermodynamics.
- A description of any thermodynamic system employs the four laws of thermodynamics that form an axiomatic basis. The first law specifies that energy can be transferred between physical systems as heat, as work, and with transfer of matter.
- The second law defines the existence of a quantity called entropy, that describes the direction, thermodynamically, that a system can evolve and quantifies the state of order of a system and that can be used to quantify the useful work that can be extracted from the system.

- In thermodynamics, interactions between large ensembles of objects are studied and categorized. Central to this are the concepts of the thermodynamic system and its surroundings.
- A system is composed of particles, whose average motions define its properties, and those properties are in turn related to one another through equations of state.
- Properties can be combined to express internal energy and thermodynamic potentials, which are useful for determining conditions for equilibrium and spontaneous processes.
- With these tools, thermodynamics can be used to describe how systems respond to changes in their environment. This can be applied to a wide variety of topics in science and engineering, such as engines, phase transitions, chemical reactions, transport phenomena, and even black holes.
- The results of thermodynamics are essential for other fields of physics and for chemistry, chemical engineering, corrosion engineering, aerospace engineering, mechanical engineering, cell biology, biomedical engineering, materials science, and economics, to name a few.

5.1.1. Branches of Thermodynamics:

- The study of thermodynamical systems has developed into several related branches, each using a different fundamental model as a theoretical (or) experimental basis, (or) applying the principles to varying types of systems.

(i) Classical Thermodynamics:

- Classical thermodynamics is the description of the states of thermodynamic systems at near-equilibrium that uses macroscopic, measurable properties. It is used to model exchanges of energy, work and heat based on the laws of thermodynamics. The qualifier classical reflects the fact that it represents the first level of understanding of the subject as it developed in the 19th century and describes the changes of a system in terms of macroscopic empirical (large scale, and measurable) parameters. A microscopic interpretation of these concepts was later provided by the development of statistical mechanics.

(ii) Statistical Mechanics:

- Statistical mechanics, also known as statistical thermodynamics, emerged with the development of atomic and molecular theories in the late 19th century and early 20th century, and supplemented classical thermodynamics with an interpretation of the microscopic interactions between individual particles or quantum-mechanical states. This field relates the microscopic properties of individual atoms and molecules to the macroscopic, bulk properties of materials that can be observed on the human scale, thereby explaining classical thermodynamics as a natural result of statistics, classical mechanics, and quantum theory at the microscopic level.

(iii) Chemical Thermodynamics:

- Chemical thermodynamics is the study of the interrelation of energy with chemical reactions (or) with a physical change of state within the confines of the laws of thermodynamics. The primary objective of chemical thermodynamics is determining the spontaneity of a given transformation.

(iv) Equilibrium Thermodynamics:

- Equilibrium thermodynamics is the study of transfers of matter and energy in systems (or) bodies that, by agencies in their surroundings, can be driven from one state of thermodynamic equilibrium to another. The term 'thermodynamic equilibrium' indicates a state of balance, in which all macroscopic flows are zero, in the case of the simplest systems (or) bodies, their intensive properties are homogeneous, and their pressures are perpendicular to their boundaries. In an equilibrium state there are no unbalanced potentials, (or) driving forces, between macroscopically distinct parts of the system. A central aim in equilibrium thermodynamics is given a system in a well-defined initial equilibrium state, and given its surroundings, and given its constitutive walls, to calculate what will be the final equilibrium state of the system after a specified thermodynamic operation has changed its walls or surroundings.

(v) Non-equilibrium Thermodynamics:

- Non-equilibrium thermodynamics is a branch of thermodynamics that deals with systems that are not in thermodynamic equilibrium. Most systems found in nature are not in thermodynamic equilibrium because they are not in stationary states, and are continuously and discontinuously subject to flux of matter and energy to and from other systems. The thermodynamic study of non-equilibrium systems requires more general concepts than are dealt with by equilibrium thermodynamics. Many natural systems still today remain beyond the scope of currently known macroscopic thermodynamic methods.

5.1.2. The Most Important Laws of Thermodynamics Are:

- Thermodynamics is principally based on a set of four laws which are universally valid when applied to systems that fall within the constraints implied by each. In the various theoretical descriptions of thermodynamics these laws may be expressed in seemingly differing forms, but the most prominent formulations are the following.
- The zeroth law of thermodynamics is defined as when two systems are each in thermal equilibrium with a third system, the first two systems are in thermal equilibrium with each other. This property makes it meaningful to use thermometers as the “third system” and to define a temperature scale.
- If two systems are each in thermal equilibrium with a third, they are also in thermal equilibrium with each other. This statement implies that thermal equilibrium is an equivalence relation on the set of thermodynamic systems under consideration. Systems are said to be in equilibrium if the small, random exchanges between them (e.g. Brownian motion) do not lead to a net change in energy. This law is tacitly assumed in every measurement of temperature. Thus, if one seeks to decide whether two bodies are at the same temperature, it is not necessary to bring them into contact and measure any changes of their observable properties in time. The law provides an empirical definition of temperature, and justification for the construction of practical thermometers.
- The zeroth law was not initially recognized as a separate law of thermodynamics, as its basis in thermodynamical equilibrium was implied in the other laws. The first, second, and third laws had been explicitly stated already, and found common acceptance in the physics community before the importance of the zeroth law for the definition of temperature was realized. As it was impractical to renumber the other laws, it was named the zeroth law, which is illustrated in the **Figure 2.**

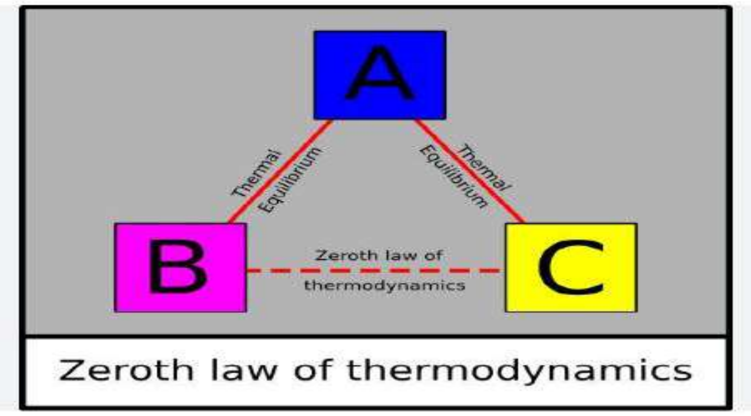


Figure 2: Illustration of Zeroth law of Thermodynamics

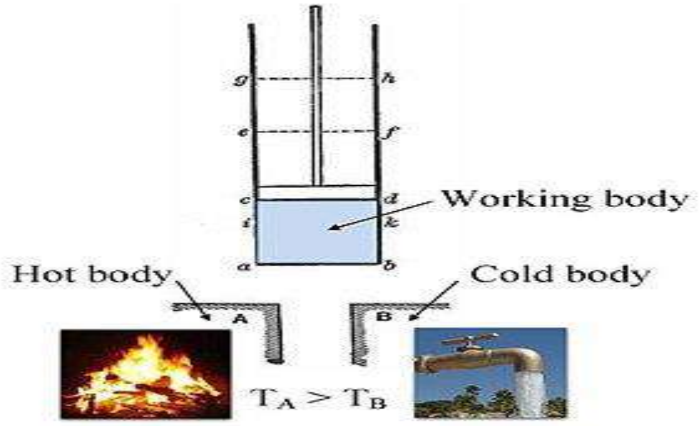


Figure 3: Schematic representation of transformation of heat from hot body, cold body and working body.

- The first law of thermodynamics or the law of conservation of energy is states that the change in a system's internal energy is equal to the difference between heat added to the system from its surroundings and work done by the system on its surroundings.
- In a process without transfer of matter, the change in internal energy, of a thermodynamic system is equal to the energy gained as heat, less the thermodynamic work, done by the system on its surroundings.
- The schematic representation of flow of heat in hot body, cold body and working body is represented in the Figure 3.

5.1.3. First law of Thermodynamics:

- The first law of thermodynamics states that the energy of the universe remains the same. Though it may be exchanged between the system and the surroundings, it can't be created or destroyed. The law basically relates to the changes in energy states due to work and heat transfer are shown in the **Figure 4.**

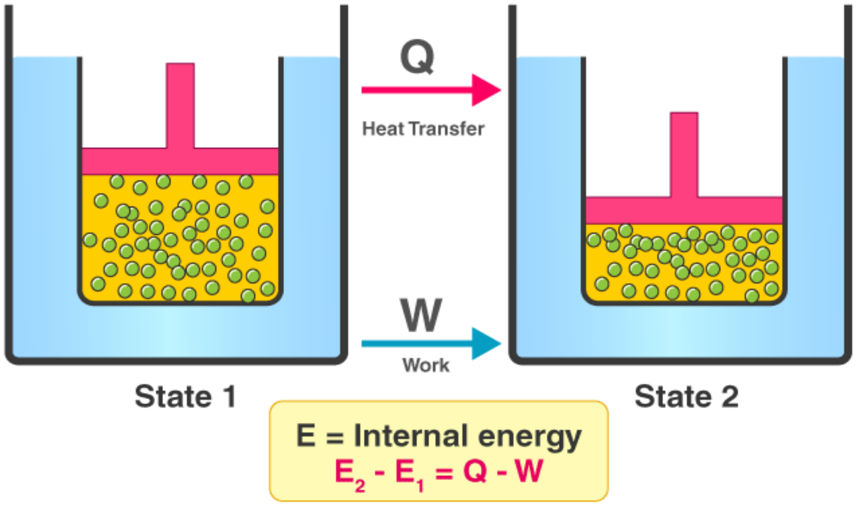


Figure 4: Schematic representation of First law of Thermodynaics

- The first law of thermodynamics can be the conversion of heat energy into work done that can be calculated by the following equation given in the Figure 5.

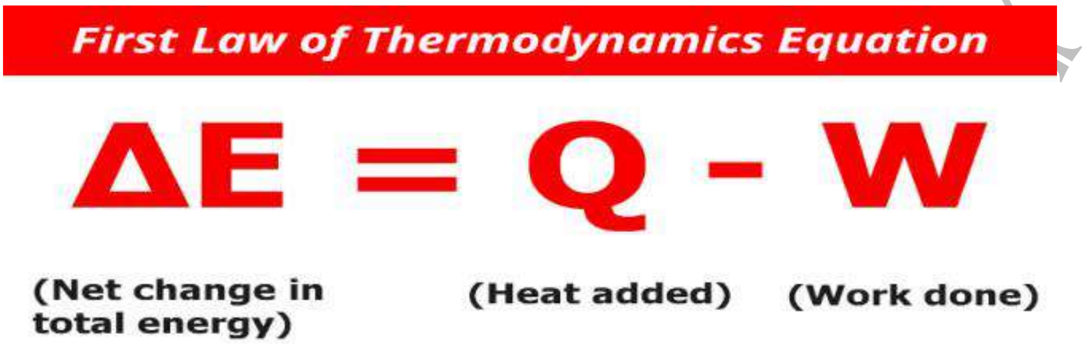


Figure 5: Indication of first Law of Thermodynamics Equation

- Where denotes the change in the internal energy of a closed system (for which heat (or) work through the system boundary are possible, but matter transfer is not possible), denotes the quantity of energy supplied to the system as heat, and denotes the amount of thermodynamic work done *by* the system on its surroundings. An equivalent statement is that perpetual motion machines of the first kind are impossible, work done by a system on its surrounding requires that the system's internal energy decrease (or) be consumed, so that the amount of internal energy lost by that work must be resupplied as heat by an external energy source or as work by an external machine acting on the system (so that is recovere(d) to make the system work continuously.

- For processes that include transfer of matter, a further statement is needed, With due account of the respective fiducially reference states of the systems, when two systems, which may be of different chemical compositions, initially separated only by an impermeable wall, and otherwise isolated, are combined into a new system by the thermodynamic operation of removal of the wall, then

$$U_0 = U_1 + U_2,$$

- Where U_0 denotes the internal energy of the combined system, and U_1 and U_2 denote the internal energies of the respective separated systems. The internal energy denoted by the term E or U.

- Adapted for thermodynamics, this law is an expression of the principle of conservation of energy, which states that energy can be transformed (changed from one form to another), but cannot be created (or) destroyed.

5.39. Multiple Choice Questions:

1. Which of the following is a branch of thermodynamics?

   A) Equilibrium thermodynamics B) Classical thermodynamics

   C) Chemical thermodynamics D) All of the above mentioned

2. What is the value of the absolute thermodynamic temperature scale?

   A) 3K B) 0K C) 1K D) 4K

3. What is the magnitude of mechanical work?

   A) product of the force and distance travelled perpendicular to the force

   B) product of the force and distance travelled parallel to the force

   C) sum of the force and distance travelled perpendicular to the force

   D) sum of the force and distance travelled parallel to the force

4. Joule was the first to prove that heat is a type of energy, laying the groundwork for the fundamental law of thermodynamics.

   A) False B) True

   C) Sometimes true sometimes false D) Neither true nor false

5. Which of the following is true for a discharging tank?

   A) the process is quasi-static B) the process is adiabatic

   C) $dQ=0$ D) all of the mentioned

6. The entropy of an isolated system can never ___________________

   A) decrease B) be zero

   C) increase D) none of the mentioned

7. Which of the following properties describe entropy?

   A) point function, intensive property B) point function, extensive property

   C) path function, extensive property D) path function, intensive property

8. When work is dissipated into internal energy, what is the change in the disorderly motion of molecules.

   A) increases B) remains the same

   C) decreases D) none of the mentioned

9. The available energy of a system ________________________ as its temperature or pressure decreases and approaches that of the surroundings.

A) remains constant B) increases

C) decreases D) none of the mentioned

10. Which of the following is true?

A) Q for reversible < Q for irreversible and work for reversible < work for irreversible

B) Q for reversible > Q for irreversible and work for reversible < work for irreversible

C) Q for reversible < Q for irreversible and work for reversible > work for irreversible

D) Q for reversible > Q for irreversible and work for reversible > work for irreversible

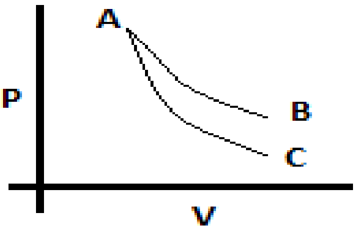
11. The first law of thermodynamics for an adiabatic process is

A) $du = \delta W$ B) du =0 C) $du = -\delta W$ D) $du = \delta H + 2\delta W$

12. A cycle tyres burst suddenly. What is the type of this process?

A) Isothermal B) Adiabatic C) Isochoric D) Isobaric

13. In the given diagram, one process is adiabatic and the other is isothermal. It can be said that process AB is adiabatic. True or False?



A) True B) False

C) Sometime true sometimes false

D) Neither true nor false

14. **Assertion A):** Thermodynamic process in nature is irreversible.

Reason (R) : Dissipative effects cannot be eliminated

A) If both assertion and reason are true but reason is correct explanation for assertion.

B) If both assertion and reason are true but reason is not correct explanation for assertion.

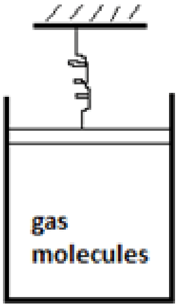
C) If assertion is true but reason is false.

D) If both assertion and reason are false

15. If 315cal of heat is given to the system, and the system does 20cal of work, find the change in internal energy.

A) 295cal B) 335cal C) 0 cal D) 335J

16. In the given system, 20J of heat is supplied to the gas molecules. The spring is initially not elongated or compressed. If the spring gets compressed by 1cm. Calculate the change in internal energy of the system. Spring constant = 200N/m. Assume piston moves slowly.



A) 19J B) -19J C) 21J D) -21J

17. Equilibrium state of a thermodynamic system is described by path variables. True or False?

A) True B) False

C) Sometimes true sometimes false D) Neither true nor false

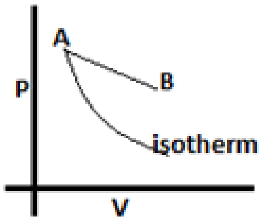
18. In which of the following processes is heat transfer equal to zero?

A) Isentropic B) Isochoric C) Isothermal D) Diathermic

19. Calculate the work done by the gas in an isothermal process from A to B. $P_A = 1Pa, V_A = 3m^3, P_B = 3Pa$.

A) 3.3J B) 3J C) -3.3J D) -4.58J

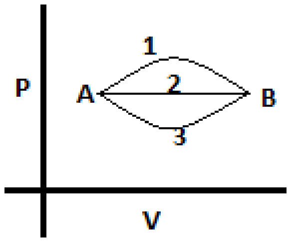
20. When the state changes from A to B, what will happen to internal energy?



A) Increase B) Decrease

C) Remain same D) Depends on value of heat supplied

21. What is the relation between heat supplied in the 3 processes?



A) $Q_1 > Q_2 > Q_3$ B) $Q_1 < Q_2 < Q_3$

C) $Q_1 = Q_2 = Q_3$ D) $Q_1 = Q_3 > Q_2$

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UNIT-6

COLLOIDS AND SURFACE CHEMISTRY & ELECTROCHEMISTRY

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UG TRB – CHEMISTRY – 2023-24

PHYSICSL CHEMISTRY - UNIT 6

COLLOIDS AND SURFACE CHEMISTRY

6.1. COLLOIDS:

6.1.1. Introduction of Colloids:

- The scientific study of colloids dates from the early 19th century.
- Among the first notable investigations was that of the British botanist **Robert Brown**.
- During the late 1820s Brown discovered, with the aid of a microscope, that minute particles suspended in a liquid are in continual, random motion.

What are colloids:

- A colloid is primarily a heterogeneous mixture in which the minute particles of one substance are dispersed in another substance, called the dispersion medium.
- The minute particles here are 1 to 1000 nanometers in diameter but they still remain suspended and do not settle at the bottom of the mixture.
- They are visible under an optical or an electron (smaller particles) microscope.

Colloids:

- It is a mixture with particle size 1-1000nm

CLASSIFICATION OF COLLOIDS

DISPERSED PHASE	DISPERSION MEDIUM	NAME OF COLLOIDAL SYSTEM	COMMON EXAMPLES
Liquid	Gas	Liquid Aerosol	Mist, clouds, fog
Solid	Gas	Aerosol	Dust, smoke
Gas	Liquid	Foam	Suds, whipped cream
Liquid	Liquid	Emulsion	Cream, milk, mayo Paints, jellies, sewage
Solids	Liquid	Sol	
Gas	Solid	Solid foam	Marshmallow
Liquid	Solid	Solid emulsion	Butter, cheese
Solid	Solid	Solid sol	Opals, some alloys

Interaction

lyophilic colloids are solvent	Lyophobic colloids are solvent hating colloids
Thermodynamically stable	Thermodynamically unstable
Precipitation in the lyophilic sol is reversible process	Precipitation in the Lyophobic sol is irreversible process
There is strong attraction force between colloids and the liquid	There is less or no attraction force between colloids and the liquid
Highly viscous	Having the same viscosity as the solvent
From a lyophilic sol	From a Lyophobic sol

Particle size

6.1.2. Classification of Colloids:

- Colloids can be classified into two types by their dispersed phase and medium. They are given below,

  1. Physical state of dispersed phase and dispersion medium.
  2. Natural of interactions between dispersed phase and dispersion medium.
  3. Type of particles of the dispersed phase.

1. Physical state of dispersed phase and dispersion medium.

- Depending upon the physical state of dispersed phase and dispersion medium whether these are solids, liquids or gases, eight types of colloidal systems are possible.

Dispersed phase	Dispersed medium	Type of colloid	Example
Solid	Solid	Solid sol	Some coloured glasses, and gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap lather

Depending upon the nature of the dispersion medium, colloidal solutions are sometimes given specific names. For example:

Dispersion Medium	Name of Colloidal Solution
Water	Hydrosols or aquasol
Alcohol	Alcosols
Benzene	Benzosols
Air	Aerosols

Classification based on Nature of Interaction between Dispersed Phase and Dispersion Medium

- Depending upon the nature of interactions between dispersed phase and the dispersion medium, the colloidal solutions can be classified into two types as:

    (i) lyophilic and

    (ii) lyophobic sols.

(i) Lyophilic colloids

- The colloidal solutions in which the particles of the dispersed phase have a great affinity (or love) for the dispersion medium, are called lyophilic colloids.

    a) These solutions are easily formed and the lyophilic colloids are reversible in nature. The reversible. If the dispersion medium is separated from the dispersed phase the sol can be again formed by simply remixing it with the dispersion medium.

    b) These sols are quite stable and cannot be easily coagulated. Examples of lyophilic colloids are gum, gelatine, starch, proteins, rubber, etc.

(ii) Lyophobic colloids

- The colloidal solutions in which there is no affinity between particles of the dispersed phase and the dispersion medium are called lyophobic colloids. Such solutions are formed with difficulty.

    (a) These sols are readily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking. Therefore, these are not stable.

    (b)Further, once precipitated, they do not form the colloidal sol by simple addition of dispersion medium. Hence, these are irreversible in nature. These sols need some stabilising agents for their preservation.

    (c) In case, the dispersion medium is water, the lyophobic sol. is called **hydrophobic colloid**. For example: the solutions of metals like Ag and Au, hydroxides $Fe(OH)_3$, metal sulphides like AS_2S_3 etc.

S.NO	**PROPERTY**	**LYOPHOBIC SOL (SUSPENSOID)**	**LYOPHILLIC SOL (EMULSOID)**
1	Preparation	Cannot be prepared easily special methods are required	Can be easily prepared by shaking or warming the substance with solvent are more stable
2	Stability	are less stable	are more stable
3	Reversibility	are irreversible	are reversible
4	Viscosity	Viscosity is nearly same as that of the solvent	Viscosity is much higher than that of solvent
5	Surface tension	Surface tension is almost same as that of solvent	Surface tension is usually low.
6	Hydration or salvation	These are less solved as the particles have less affinity for the solvent	These highly solved as the particles have great affinity for solvent
7	Charge	The particles carry a characteristic charge either positive or negative	The particles have little charge or no charge at all.
8	Visibility	Particles can be seen under microscope	Particles cannot be seen under microscope
9	Coagulation or precipitation	Precipited by low concentration of electrolysis	Precipited by high concentration of electrolysis
10	Tyndal effect	More scattering	Less scattering
11	Migration in electric filed	Migrate towards anode or cathode as these participles	Mayor may not migrate carry charge
12	General example	Mostly of inorganic nature	Mostly of organic nature

Classification Based on Type of Particles of Dispersed Phase:

- Depending upon the type of the particles of the dispersed phase, the colloids are classified as:

  1) Multimolecular colloids
  2) Macromolecular colloids
  3) Associated colloids.

1) Multimolecular Colloids:

- When on dissolution, atoms or smaller molecules of substances (having diameter less than 1 nm) aggregate together to form particles of colloidal dimensions, the particles thus formed are called **multimolecular colloids.**
- Therefore, in these sols the dispersed phase consists of aggregates of atoms or molecules with molecular size less than 1 nm.
  - ➢ **For example:** sols of gold atoms and sulphur (S_8) molecules.

    In these colloids, the particles are held together by van der Waals forces.

2) Macromolecular Colloids:

- These are the substances having big size molecules (called macro molecules) which on dissolution form solution in which the dispersed phase particles have size in the colloidal range.
- **Naturally occurring macro-molecules** are starch, cellulose, proteins, enzymes, gelatin etc.
- **Artificial macro-molecules** are synthetic polymers such as nylon, polythene, plastics, polystyrene etc.
- Since these macromolecules have large sizes comparable to those of colloidal particles, the solutions of such molecules are called macromolecular colloidal solutions.
- Thus, the common examples of macromolecular colloids are starch, cellulose, proteins, plastics, etc.

3) Associated Colloids:

- These are the substances which when dissolved in a medium behave as normal electrolytes at low concentration but behave as colloidal particles at higher concentration due to the formation of aggregated particles.

- The aggregate particles thus formed are called **micelles**.
  - **For example:** In aqueous solution soap (sodium stearate) ionises as:

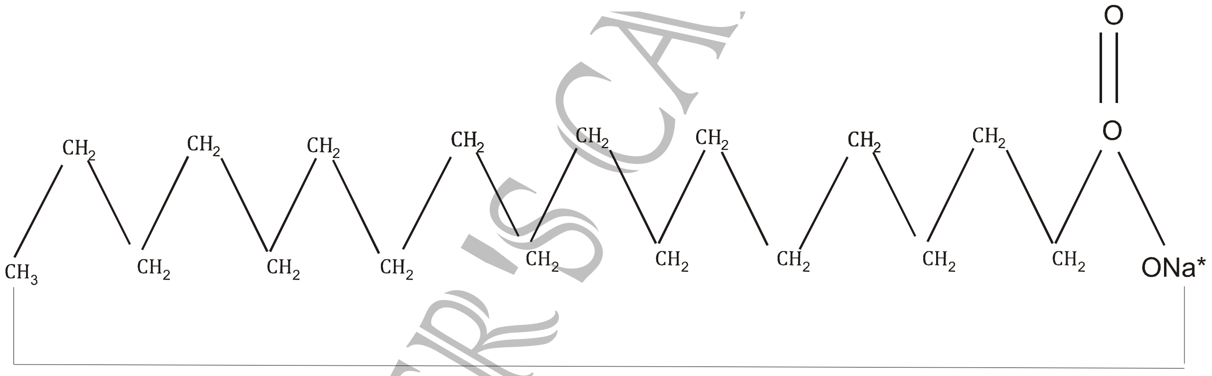
$$C_{17}H_{35}COONa \Leftrightarrow C_{17}H_{35}COO^- + Na^+$$

- In concentrated solution, these ions get associated to form an aggregate of colloidal size. The colloidal behaviours of such substances is due to the formation of aggregates or clusters in solutions. Such aggregated particles are called **micelles**.
- Thus, micelles are the cluster or aggregated particles formed by association of colloids in solution. The common examples of micelles are soaps and detergents.
- The formation of micelles takes place above a particular temperature called **Kraft** temperature (T_k) and above a particular concentration called **critical** micellization concentration (CMC).
  - **For example:** CMC for soaps is about 10^{-4} to 10^{-3} mol L^{-1}

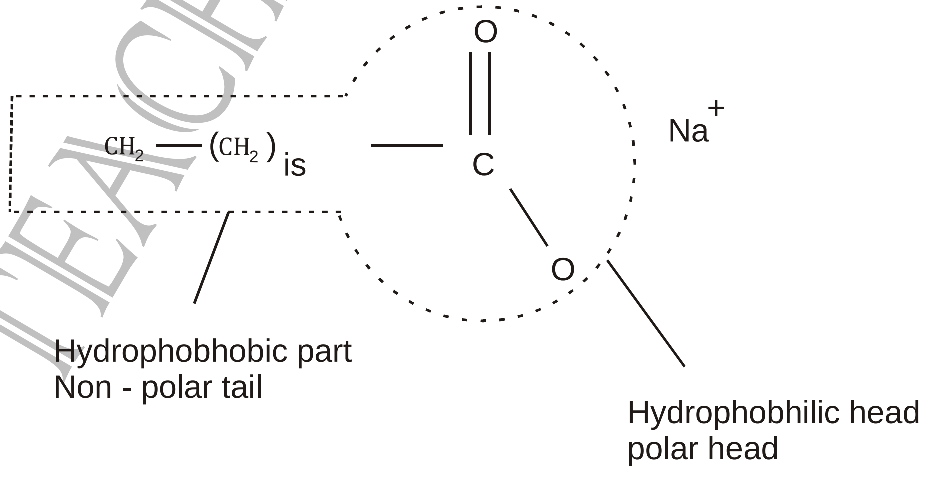
  On dilution, these colloids revert back to individual ions.

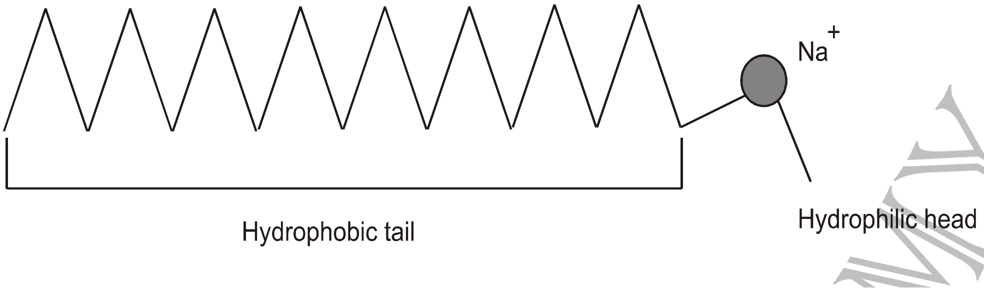
Mechanism of Micelle Formation:

These two parts soaps are represented as:



Sodium stearate $C_{17}H_{35}COO^- Na^+$
of simply as





- Micelles are generally formed by the aggregation of several ions or molecules with lyophobic as well as lyophilic parts. The micelle may contain as many as 100 molecules or more. When sodium stearate is dissolved in water, it gives Na^+ and CH_3COO^- ions.

$$C_{17}H_{35}COONa \Leftrightarrow C_{17}H_{35}COO^- + Na^+$$

- The stearate ions associate to form ionic micelles of colloidal size. The stearate ion, $C_{17}H_{35}COO^-$ consists of two parts:

1) a non-polar part which consists of long chain hydrocarbon part. It is called non-polar tail. This part is insoluble in water but soluble in oil or grease. It is also called water repelling or hydrophobic part.

2) a polar group which consists of carboxylate ion, COO^-. It is called polar-ionic head. It is soluble in water and insoluble in oil or grease. It is water attracting or hydrophilic part.

a) The stearate ions are therefore, present on the surface with their COO^- groups in water and the hydrocarbon tail staying away from it and remains at the surface.

b) Inside water, these molecules have a unique orientation which keeps the hydrocarbon portion out of water.

c) At critical micelle concentration, the anions are pulled into the bulk of the solution and form a cluster of molecules in which the hydrocarbon tails are in the interior of the cluster and ionic ends are at the surface of the cluster. This formation is called **micelle formation** and the aggregate thus formed is known as **ionic micelle.**

Examples of Micelles are:

(i) Sodium palmitate $\left[C_{15}H_{31}COONa\right]$

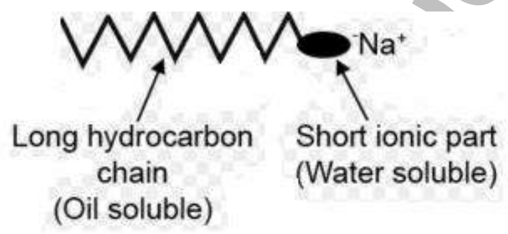
(ii) Cetyl trimethyl ammonium bromide $CH_3\left(CH_2\right)_{15}\left(CH_3\right)_3 N^+Br^-$

(iii) Sodium lauryl sulphate $\left[CH_3\left(CH_2\right)_{11} SO_3O^-Na^+\right]$

- In case of detergents e.g., sodium lauryl sulphate, $CH_3\left(CH_2\right)_{11}OSO_3^{-}Na^{+}$, the polar group is SO_4^{2-} along with the long hydrocarbon chain.Therefore, the mechanism of micelle formation is same as that of soaps.

Multimolecular colloids	**Macromolecular colloids**	**Associated colloids**
They consist of aggregates of atoms or molecules which generally have diameter less than 1nm.	They consist of large size molecules	They consist of aggregation of a large number of ions which behave as colloidal size
The atoms of molecules are held by weak van der waal forces	The molecules are flexible and take any shape.	They behave as normal electrolyte at low concentration and behave as colloidal only at high concentration.
Their molecules masses are not very high	They have high molecular masses.	Their molecular masses are generally high.
They have usually lyophillic character	They have usually lyophobic character	Their molecular contain both lyophilic and lyophobic groups.

Cleansing Action of Soap:



1) The cleansing action of soap is due to its tendency to act as micelle and form emulsions.

2) A soap is composed of long chain of alkyl group called tail and a polar part COO^{-} ion called head.

3) The dirt in the cloth is due to the presence of dust particles in fat or grease which stick to the cloth.

4) When the cloth is dipped in aqueous soap solution, the soap and the dirt come in contact with each other.

- Mitigate against the impacts of heat and chlorides in association with other corrosion-impacting factors
- Use treated and coated wood products if they will be in contact with soils or in waterfront environments
- Use coatings appropriate for the intended use to protect structures
- Apply proper construction and maintenance practices, accompanied by appropriate material selection and surface treatments, to reduce the impacts of ultraviolet degradation on asphaltic materials in pavements and roofs
- Use appropriate concrete cover and coatings to minimize spalling in reinforced concrete structures

Exercise Questions: VI

1. Conductivity (unit Siemen's S) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel then the unit of the constant of proportionality is **[2002]**

(a) $Sm\ mol^{-1}$

(b) $Sm^2\ mol^{-1}$

(c) $S^{-2}m^2\ mol$

(d) $S^2m^2\ mol^{-2}$.

6.5. MULTIPLE CHOICE QUESTIONS

1. Which is not correct regarding the adsorption of a gas on surface of solid?

A) on increasing temperature adsorption increases continuously

B) enthalpy and entropy change is –ve

C) adsorption is more for some specific substance

D) reversible

2. Position of non-polar and polar part in micelles:

A) polar on outer surface and non-polar on inner surface

B) polar on inner surface and non-polar on outer surface

C) distributed over all the surface

D) are present on the surface only

3. Which of the following forms cationic micelles above certain concentration?

A) sodium dodecyl sulphate B) sodium acetate

C) urea D) cetyltrimethyl ammonium bromide

4. The statement not applicable to chemisoption is that it is

A) highly specific B) independent of temperature

C) irreversible D) slow

5. The blue colour of water in the sea is due to

A) scattering of blue light by water molecules

B) reflection of blue sky by sea water

C) refraction of blue light by the impurities in sea water

D) adsorption of other colours, except the blue colour by water molecules

6. Which of the following is correct for lyophilic sol?

A) irreversible sol B) formed from inorganic substances

C) readily coagulated by addition of electrolyte D) self stabilized

7. Rate of physisorption increases with

A) decrease in temperature B) increase in temperature

C) decrease in pressure D) decrease in surface area

8. Milk is a colloid in which

A) liquid is dispersed in liquid B) gas is dispersed in liquid

C) sugar is dispersed in water D) solid is dispersed in liquid

9. Physical adsorption is inversely proportional to

A) temperature B) volume C) concentration D) all of these

10. The migration of colloidal particle under the influence of electric field towards an electrode is known as

A) electrophoresis B) electro-osmosis

C) Tyndall effect D) Brownian movement

11. Butter is a colloidal solution of

A) solid–solid B) liquid–solid C) solid–liquid D) gas–solid

12. How many layers are adsorbed in chemical adsorption?

A) zero B) one C) two D) infinite

13. In the adsorption of oxalic acid on activated charcoal, the activated charcoal is known as

A) adsorber B) adsorbent C) absorber D) adsorbate

14. Adsorbed acetic acid on activated charcoal is

A) adsorbate B) adsorber C) absorber D) absorbent

15. Which one of the following forms micelles in aqueous solution above certain concentration?

A) dodecyl trimethyl ammonium chloride B) glucose

C) urea D) pyridinium chloride

16. What is the name of a phenomenon in which both adsorption and absorption takes place?

A) chemisorption B) physisorption C) desorption D) sorption

17. What is the equation form of Langmuir isotherm under high pressure?

A) x/m = a/b B) x/m = a.p C) x/m = 1/a.p D) x/m = b/a

18. Which of the following is a lyophillic colloidal solution?

A) aqueous starch solution B) aqueous protein solution

C) gold sol

D) polymer solutions in some organic solvents

19. Which one of the following statements is not correct?

A) physical adsorption decreases with increase in the temperature

B) physical adsorption is multilayered

C) activation energy of physical adsorption is very high.

D) enthalpy change of physical adsorption is about $20\ kJ\ mol^{-1}$.

20. Which one of the following is an example of adsorption?

A) ammonia in contact with water B) anhydrous $CaCl_2$ with water

C) silica gel in contact with water vapours D) all of these.

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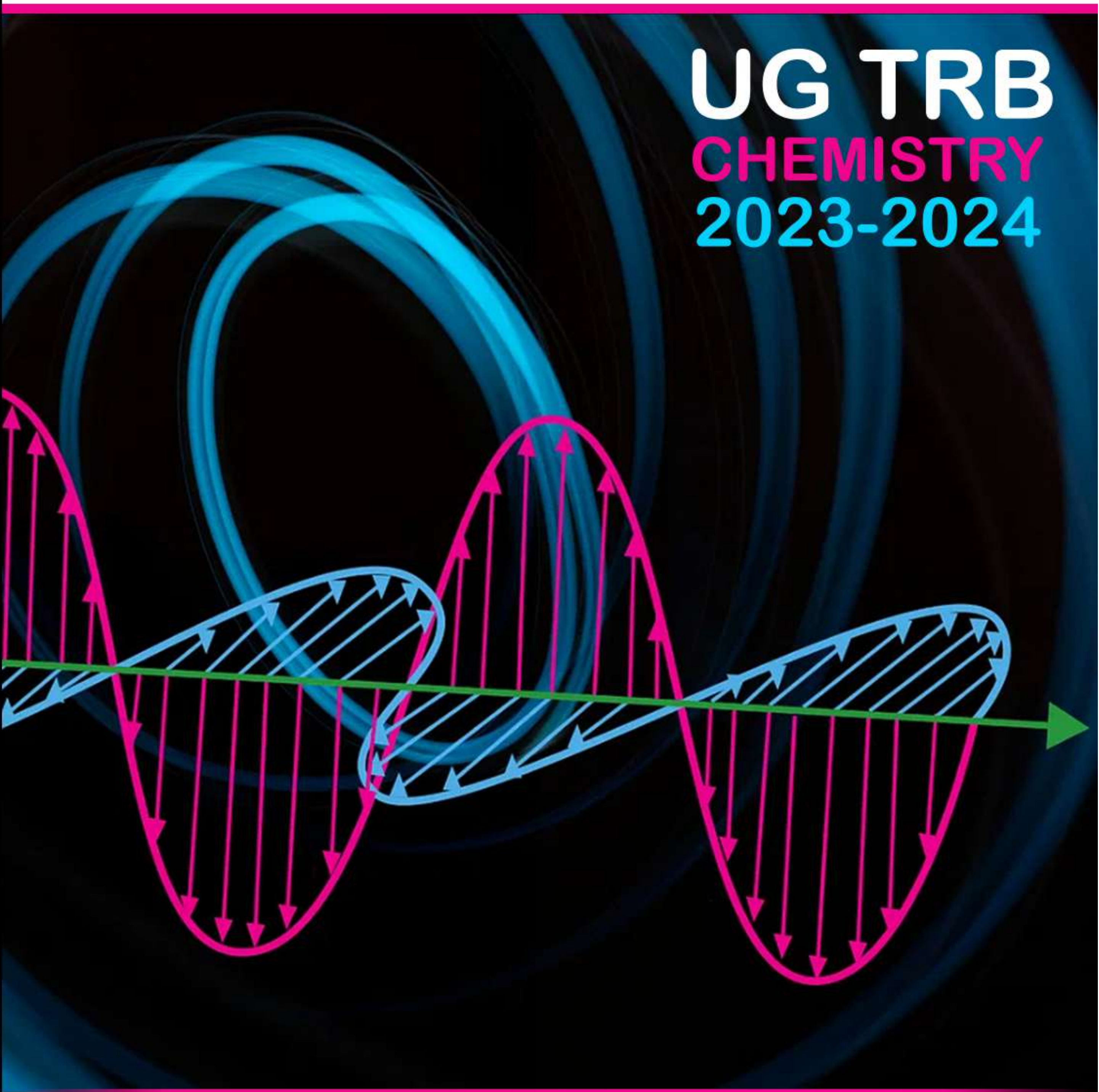

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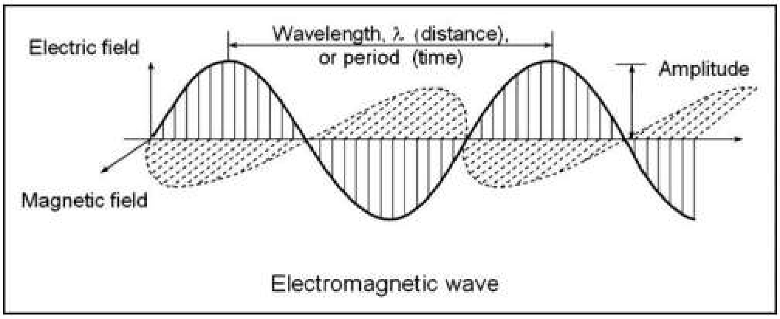
PHYSICAL CHEMISTRY UNIT - 7 - SPECTROSCOPY

7.1. ELECTROMAGNETIC SPECTRUM:

- The branch of science that deals with the study of electromagnetic radiation and its interaction with matter is called *spectroscopy*.
- Spectroscopy gives information about the energy difference between energy levels in atoms or molecules, amount of energy absorbed or emitted and the physical constants of molecules derived therein.
- *Electromagnetic spectrum* is the entire distribution of electromagnetic radiation (EMR) according to their wavelength or frequency
- In vacuum, EMR travel with the speed of light ($c = 3\times10^8$ m/s), however they do so with a wide range of wavelengths, frequencies and energies.
- Electromagnetic radiation or light propagates in waves similar to water waves in ocean. EMR consists of alternating electric and magnetic fields.
- An electric field of the Electromagnetic Radiation interacts with the induced electric field created by charged particles of matter (Rotational, Vibrational and Electronic spectroscopy).
- A magnetic field of the EMR interacts with magnetic field created by electron and proton in nucleus (NMR and EPR spectroscopy).



The electromagnetic waves are described by following three physical properties:

7.1.1. Frequency

- The number of waves passing through at a given point of time is called frequency.
- It is denoted by ν (nu). Its unit is Hertz (Hz) or s^{-1}.

7.1.2. Wavelength

- The distance between two crust and trough (high and low amplitude) is called as wavelength.
- It is denoted by λ (lambda) and its units are °A, cm, m, nm, etc.

7.1.3. Wave Number

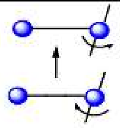
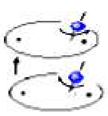
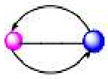
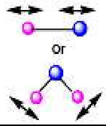
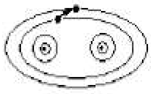
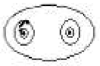
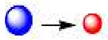
- The number of wavelengths per unit distance, typically centimeters.

$$\bar{\nu} = \frac{1}{\lambda}$$

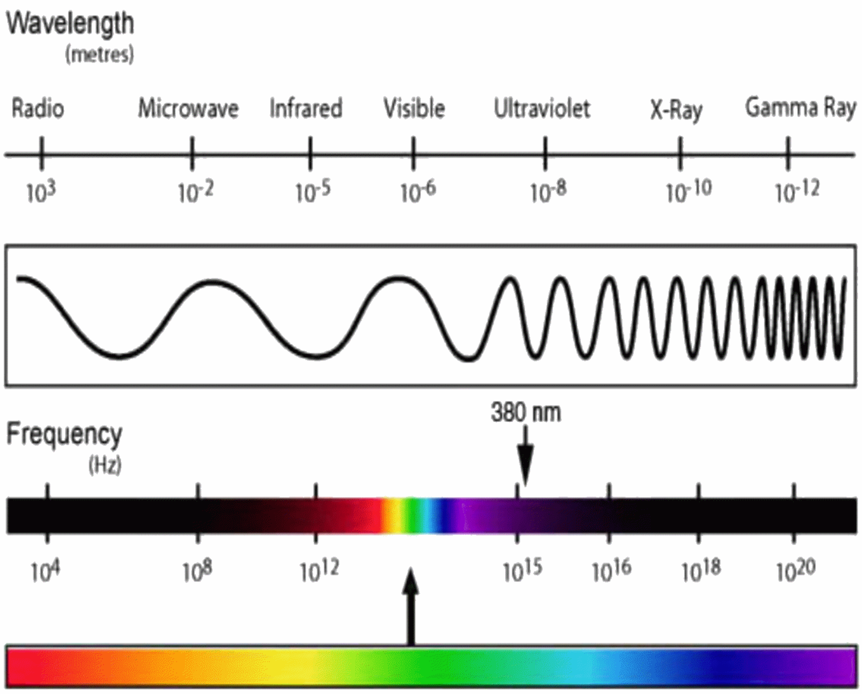
- Photon Energy – Energy associated with a single photon. It is proportional to the frequency of light (Photon – light packet or packet of electromagnetic radiation).

7.2. DIFFERENT REGIONS OF SPECTRA

- EMR is divided into different regions based on the type of the atomic or molecular transition that gives rise to the absorption or emission of photons.
- The boundaries are not precise but the molecular processes associated with each region are different.

	Change of spin		Change of orientation	Change of configuration	Change of electron distribution		Change of nuclear configuration
	radiowave NMR	ESR	Microwave	Infra-red	Visible and UV	X-ray	γ- ray
							
$\bar{\nu}$ in cm^{-1}		10^{-2}	1	100	10^4	10^6	10^8
λ	10m	100cm	1cm	100μm	1μm	10nm	100pm
ν in Hz	3×10^6	3×10^8	3×10^{10}	3×10^{12}	3×10^{14}	3×10^{16}	3×10^{18}
E in J/mol	10^{-3}	10^{-1}	10	10^3	10^5	10^7	10^9

Name of the Region	Frequency (Hz)	Wavelength	Name of the spectroscopy	Molecular process	Energy
Radiofrequency	3×10^{6} - 3×10^{10}	10 m – 1 cm	NMR and EPR	Reversal of spin of nucleus or electrons	0.001 – 10 J/mol
Microwave	3×10^{10} - 3×10^{12}	1 cm – 100 μm	Rotational	Rotation of molecules	100 J/mol
Infra-red	3×10^{12} - 3×10^{14}	100 μm – 1 μm	Vibrational and Raman	Vibration of atoms and molecules	10^{4} J/mol
Ultra-violet and Visible	3×10^{14} - 3×10^{16}	1 μm – 10 nm	Electronic	Electronic transitions (Valence electrons)	Hundreds of kJ/mol
X-ray	3×10^{16} - 3×10^{18}	10 nm – 100 pm	X-ray	Electronic transitions (Inner core electrons)	10,000 kJ/mol
γ-ray	3×10^{18} - 3×10^{20}	100 pm – 1 pm	Mossbauer	Rearrangement of nuclear particles	10^{9} – 10^{11} J/gm of atom



Regions in Electromagnetic Radiation

7.2.1. Radio Waves

- Radio waves are the types of electromagnetic waves that are produced by the accelerated motion of charges in conducting wires or oscillating electric circuits. They are extensively used in radio and television communication systems.

7.2.1.1. Properties of Radio Waves

- The frequency range lies between 500 kHz and 1000 MHz
- The wavelength range lies between 10^{-2} m and 10^{4} m.
- The radio waves can be reflected, refracted and diffracted

7.2.1.2. Uses of Radio Waves

- Amplitude modulated (AM) (Frequency 530 to 1710 kHz) is used in ground wave propagation.
- Short waves (SW - frequency 1710 kHz to 54 MHz) are used in sky wave communication.
- Television waves have the frequency ranging from 54 to 890 MHz
- Frequency modulated (FM) with the band of frequency ranging from 88 to 108 MHz are used for FM communication
- Ultra-high frequency waves (UHF - frequency 300 to 3000 MHz) are used in cellular phone communication.

7.2.2. Microwaves

- The microwaves are short-wavelength radio waves. These waves are produced by special vacuum tubes, called Gunn diodes, magnetrons, and klystrons.
- The frequency range of microwaves lies between 1 GHz and 300 GHz

7.2.2.1 Uses of Microwaves

- Due to their short wavelengths, these waves are used in radar system for aircraft navigation.
- Used to detect speeds of a tennis ball, Cricket ball, automobiles, etc
- Used in microwave ovens

7.2.3. Infrared Waves

- Infrared waves are produced by hot bodies, that is, the vibrations of atoms and molecules. Such waves have low frequency.

7.2.3.1. Properties of Infrared Waves

- The frequency range lies between 10^{11} Hz and 10^{14} Hz
- The wavelength range lies between 1m and 700 nm.
- They are also known as heat waves.
- They cannot be detected by human eyes, but snakes and certain insects can detect these waves.
- These waves are readily absorbed by particles like carbon dioxide, ammonia, water molecules, etc After getting absorbed by the above-mentioned particles, they heat their surrounding environment.
- Infrared waves are also responsible for maintaining Earth’s average temperature through the greenhouse effect.

7.2.3.2. Uses of Infrared Waves

- An infrared lamp is used in physical therapy to treat muscular strain.
- It is used as detectors, in earth satellites, in order to observe the growth of crops and for security purposes
- It provides electrical energy to satellites by using solar cells.
- It is used to take photographs during fog and smoke.
- It is used to study molecular structure by means of an infrared absorption spectrum.

7.2.4. Visible Rays

- Visible rays are a range of electromagnetic spectrum produced by atomic excitation. They are the only range that is sensitive to human eyes, as the visible light emitted or reflected from the objects makes us see the world around us. It is detected by the eyes, photocells, and photographic films. The frequency range lies between 4×10^{14} Hz and 7×10^{14} Hz. The wavelength range lies between 700 and 400 nm.

7.2.5. Ultraviolet Rays

- Ultraviolet rays are produced by the sun, special lamps, and very hot bodies. The frequency range lies between 8×10^{14} Hz and 5×10^{16} Hz. The wavelength range lies between 400 nm and 0.6 nm.

7.2.5.1. Uses of Ultraviolet rays

- Used in LASIK (Laser-assisted in situ keratomileusis), Eye surgery, that requires high Precision focused narrow beam of ultraviolet rays.

- Used in UV lamps that are used to kill germs in water purifiers
- Used for the destruction of bacteria in hospitals and laboratory
- Used in sterilization of surgical instruments
- Exposure to ultraviolet radiation is harmful to both humans and aquatic animals. Thus ozone layer restricts the entry of ultraviolet rays into the Earth's atmosphere.

7.2.6. X-rays

- X-rays are produced in a modern x-ray tube, when a metal target is bombarded with high-energy electrons. The frequency range lies between 10^{16} Hz and 10^{21} Hz. The wavelength range lies between 10 nm and 10^{-4} nm. These waves are detected by photographic films, Geiger tubes, and ionization chambers.
- Exposure to X-rays can lead to the destruction of living tissues and can also be responsible for mutation (alteration of the genetic code) in extreme cases. Hence, it is advised for pregnant women to stay away from x-ray rooms.

7.2.6.1. Uses of X-rays

- It is used as a diagnostic tool in detecting cracks, fractures and displacements in bones.
- Used in treatment for certain forms of cancer, under the name of radiotherapy
- Used in engineering to detect faults, for crack, flaws, and holes
- Used to detect pearls in oysters, defect in rubber tires, and gold

7.2.7. Gamma Rays

- This is the high-frequency rays which is produced in nuclear reactions and is emitted by radioactive nuclei.

7.2.7.1. Properties of gamma rays

- The Frequency range lies between 10^{18} Hz and 10^{22} Hz.
- The Wavelength range lies between 10^{-10} m and 10^{-14} m.
- Waves show the properties like phosphorescence, fluorescence, polarization, and diffraction
- They have a very high penetrating power

7.2.7.2. Uses of Gamma Rays

- It is used for cancer therapy, by destructing cancer cells
- Its provides important information about the nuclear structure

Exercise Questions: 1

1. Absorption spectrum results when an electron in an atom undergoes a transition from

   (A) higher energy level to a lower one (B) lower energy level to a higher one

   (C) intermediate levels (D) All of the above

2. The energy of a photon is given by

   (A) h/ν (B) ν/h (C) 1/hν (D) hν

3. The spectra can be broadly classified into two categories. They are _____________-

   (A) atomic and molecular spectra (B) atomic and electronic spectra

   (C) molecular and electronic spectra (D) none of the above

4. Select the correct statement from the following options:

   (A) molecular spectra arises from the transition of an electron between the molecular energy levels

   (B) In molecular transitions, electronic, rotational and vibrational transitions occurs.

   (C) molecular spectra is more complicated than atomic spectra

   (D) all of the above

5. The necessary condition for the absorption spectra is that

   (A) hν should be greater than the energy difference

   (B) hν should be smaller than the energy difference

   (C) hν should be equal to the energy difference

   (D) none of the above

6. The different types of energy associated with a molecule are

   (A) electronic energy (B) vibrational energy

   (C) rotational energy (D) all of the above

7. During the motion, if the centre of gravity of molecule changes, the molecule possess…..

   (A) electronic energy` (B) rotational energy

   (C) translational energy (D) vibrational energy

8. The correct order of different types of energies is _____________.

   (A) $E_{el} >> E_{vib} >> E_{rot} >> E_{tr}$ (B) $E_{el} >> E_{rot} >> E_{vib} >> E_{tr}$

   (C) $E_{el} >> E_{vib} >> E_{tr} >> E_{rot}$ (D) $E_{tr} >> E_{vib} >> E_{rot} >> E_{el}$

9. The region of electromagnetic spectrum for Nuclear Magnetic Resonance is ___________.

(A) Microwave (B) Radiofrequency

(C) Infrared (D) UV rays

10. Which of the following is an application of molecular spectroscopy?

(A) Structural investigation

(B) Basis of understanding of colours

(C) study of energetically excited reaction products

(D) all of the above

7.3. MICROWAVE SPECTRA OF DIATOMIC MOLECULES, ROTATIONAL CONSTANTS AND SELECTION RULES

- The microwave region ($\lambda = 1$ cm – 100 μm; $\nu = 3\times10^{10} - 3\times10^{12}$ Hz and $\Delta E = 100$ J/mole) of the electromagnetic radiation is concerned with the study of rotating molecules.
- The rotation of a three-dimensional body is conveniently resolved into rotational components about three mutually perpendicular directions through the centre of gravity – the principal axis of rotation. Hence the body has three principal moments of inertia and designated as I_A, I_B and $I_{(C)}$
- Three directions of rotation may be taken as

  (i) About the bond axis (I_A)

  (ii) End-over-end rotation in the plane of the paper (I_B)

  (iii) End-over-end rotation at right angles to the plane (I_C)

7.3.1. Types of Molecules:

- Molecules are classified into groups according to the relative values of their three principal moments of inerti(a) They are as follows:

7.3.1.1. Linear molecules

- In linear molecules, all the atoms are arranged in a straight line.

Example:

HCl, OCS

- The moment of inertia, I_B=I_C and I_A is very small.

$$I_B = I_C \text{ and } I_A = 0$$

7.3.1.2. Symmetric Top

- Consider a molecule such as methyl fluoride, where the three hydrogen atoms are bonded tetrahedrally to the carbon.
- The end-over-end rotation in and out of the plane are identical (I_B=I_C).
- The moment of inertia about the C-F bond axis (main rotational axis) is not negligible, because it involves the rotation of three comparatively massive hydrogen atoms off this axis. Such a molecule spinning about this axis can be imagined as a top and hence the name.

$$I_B = I_C \neq I_A \text{and } I_A \neq 0$$

- Prolate symmetric top molecules Ex: CH_3F

$$I_B = I_C > I_A$$

- Oblate symmetric top molecules Ex: BCl_3

$$I_B = I_C < I_A$$

7.3.1.3. Spherical Top Molecules

- When a molecule has all three moments of inertia identical, it is called a spherical top.

$$I_B = I_C = I_A$$

- They have no dipole moment owing to their symmetry and hence no rotational spectrum. Ex: CH_4

7.3.1.4. Asymmetric Top Molecules

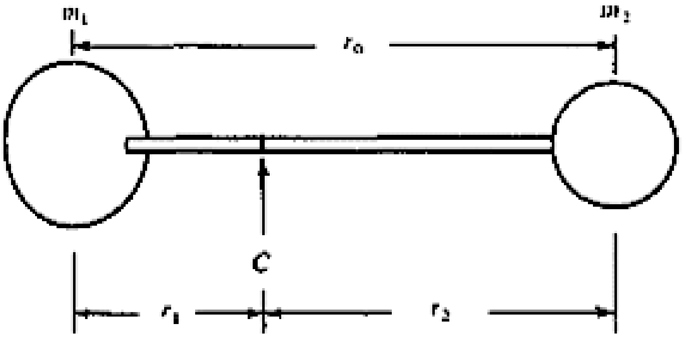
- These molecules have all three moments of inertia different. Majority of molecules fall under this category.

$$I_B \neq I_C \neq I_A$$

Example: water, vinyl chloride

7.3.2. Rigid Rotor

- Let us consider a simple diatomic molecule of masses m1 and m2 and they are joined by rigid bar (the bond) whose length is,



$$r_0 = r_1 + r_2 \qquad (1)$$

- The molecule rotates end-over-end about a point c, the centre of gravity, this is defined by the moment

$$m_1 r_1 = m_2 r_2 \qquad (2)$$

- The moment of inertia about c is,

$$I = \mu r_0^2 \qquad (3)$$

- Where, μ - reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

- From equ (3), the moment of inertia is defined in terms of atomic masses and bond length.
- From Quantum chemistry, the rotational energy expression for a rigid diatomic molecule is shown in equ (4).

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \qquad \text{Joules} \qquad (4)$$

- Where, h - Planck's constant
- I - moment of inertia
- J - rotational quantum number (J = 0, 1, 2,……….)
- From the solution of Schrodinger equation, it is evident that J can take up integral values and hence the rotational energy is quantized.
- In the rotational region, spectra are usually discussed in terms of wave number, so it is useful to consider energies expressed in these units:

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1) \qquad cm^{-1} \qquad (5)$$

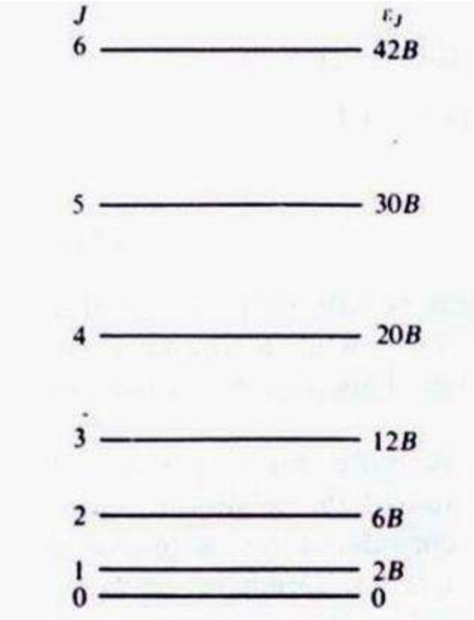
c - velocity of light in cms^{-1}

Equ (5) is abbreviated to

$$\varepsilon_J = BJ(J+1) \qquad cm^{-1} \qquad (6)$$

- Where B is the rotational constant and is expressed as

$$B = \frac{h}{8\pi^2 Ic} \quad cm^{-1} \qquad (7)$$



The allowed rotational energy levels of a rigid diatomic molecule

- For J = 0, we have $\varepsilon_J = 0$ and the molecule is not rotating.
- For J = 1, $\varepsilon_J = 2B$ and a rotating molecule then has its lowest angular momentum.
- And for each J value the ε_J increases and there is no limit to the rotational energy the molecule may have.
- Let us consider the differences between the levels to discuss the spectrum.
- Let the molecule be in the J = 0 state, the ground rotational state, where no rotation occurs.
- The molecule absorbs incident radiation and goes to J = 1 state.
- The energy absorbed,

  $$\varepsilon_{J=1} - \varepsilon_{J=0} = 2B - 0 = 2B \quad cm^{-1}$$

  and therefore,

  $$\bar{\nu}_{J=0\to J=1} = 2B \quad cm^{-1} \qquad (8)$$

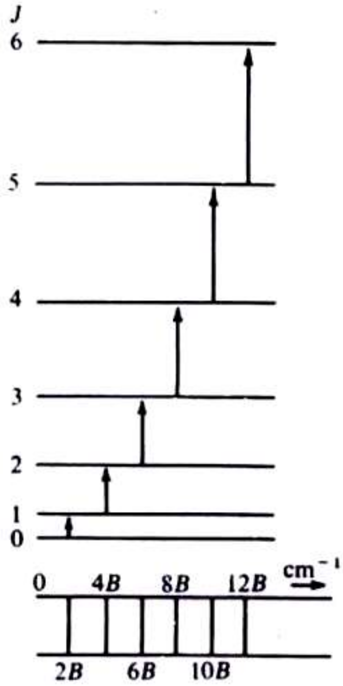
- This indicates that an absorption line occurs at 2B cm^{-1}.
- Similarly, a molecule is raised from the J = 1 to J = 2 level by absorption of energy,

  $$\bar{\nu}_{J=1\to J=2} = 6B - 2B = 4B \quad cm^{-1} \qquad (9)$$

- In general, to raise the molecule from the state J to state J + 1, we would have,

  $$\bar{\nu}_{J\to J+1} = 2B(J+1) \quad cm^{-1} \qquad (10)$$

- Thus, a stepwise raising of the rotational energy results in an absorption spectrum consisting of lines at 2B, 4B, 6B,........cm^{-1}, while a similar lowering would result in an identical emission spectrum.



Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum

7.3.3. Intensities Of The Spectral LineS:

- The relative intensities of the spectral lines require knowledge of the relative probabilities of transition between the various energy levels.
- For forbidden transitions, the transition probability is zero. The probability of all changes with $\Delta J = \pm 1$ is the same.
- The line intensities will be directly proportional to the initial number of molecules in each level.
- In general, each energy level is (2J+1)-fold degenerate. Although the molecular population in each level decreases exponentially, the number of degenerate levels available increases rapidly with J. The total relative population energy E_J is,

$$\text{Population} \propto (2J+1)\exp\left(-E_J/kT\right) \qquad (11)$$

- Transitions between levels with very low or very high J values will have small intensities while the intensity will be a maximum at or near the J value given by following equ.

$$J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2} \qquad (12)$$

7.3.4. Effect of Isotopic Substitution

- When a particular atom in a molecule is replaced by its isotope, the resulting substance is identical chemically with the original. This process is known as isotopic substitution. On isotopic substitution, there is change in total mass and hence in the moment of inertia and B value for the molecule.
- If we designate the ^{13}C molecule with a prime we have B > B'. This change is reflected in the rotational energy levels of the molecule and shows that the relative lowering of the ^{13}C levels with respect to those of ^{12}(C)

$$\frac{B}{B'} = \frac{h}{8\pi^2 Ic} \cdot \frac{8\pi^2 I' c}{h} = \frac{I'}{I} = \frac{\mu'}{\mu} \qquad (13)$$

- Where μ is the reduced mass, and the internuclear distance is considered unchanged by isotopic substitution.

7.3.5. Selection Rule

- The molecule must possess a permanent dipole moment to show microwave spectra.
- If the molecule is homonuclear, there will be no dipole component change during the rotation and hence no interaction with radiation.

  HCl, CO, NO - Microwave active

  N_2, O_2, H_2 - Microwave inactive

- For diatomic molecule, we considered transition in which J changes by one unit and all other transitions (ΔJ≠1) are spectroscopically forbidden.

  Selection rule $\Delta J = \pm 1$ 14)

- If the molecule is asymmetric (heteronuclear) the microwave spectrum is observed.
- Microwave studies can give directly an estimate of the abundance of isotopes by comparison of absorption intensities.

Exercise Questions: 2

1. Which radiation has rotational phenomenon?

   (A) Microwave (B) Infrared (C) X-rays (D) Visible

2. Which molecule is not symmetric top?

   (A) H_2O (B) BCI_3 (C) CH_3Cl (D) BF_3

3. When all the three principal moments of inertia of a molecule are equal, it is called

(A) Symmetric top	(B) Prolate symmetric top
(C) Asymmetric top	(D) Spherical top

4. Which information is spectra of a obtained from rotational molecule?

(A) Molecular structure	(B) Dipole moment
(C) Atomic mass	(D) All of A, B, and C

5. Which molecule is Microwave inactive?

(A) N_2 (B) CO (C) H_2O (D) HC ≡ CH

6. Which molecules do not show microwave spectrum?

(A) Spherical tops	(B) Symmetric tops
(C) Linear molecules	(D) Asymmetry tops

7. The rotational spectroscopy cannot be applied to detect

(A) Moment of inertia	(B) Interstellar space
(C) Molecular groupings	(D) Bond length

8. Condition for a molecule to be microwave active is

(A) change in dipole moment	(B) change in polarisability
(C) permanent dipole moment	(D) all of the above

9. Which of the following molecules show microwave activity?

(A) H_2 (B) CO_2 (C) SF_6 (D) CH_3Cl

10. Intensity of microwave spectral lines

(A) is same	(B) increases with increase in energy
(C) increases with decrease in energy	(D) goes through maximum

7.4. VIBRATIONAL SPECTROSCOPY OR INFRA-RED SPECTROSCOPY (IR SPECTROSCOPY)

- The infra-red region of the electromagnetic radiation covers a frequency of 3×10^{12} -3×10^{14} Hz and a wavelength of 100 μm -1 μm with an energy difference of 10^4 J/mole. The atoms in a molecule do not remain in fixed relative positions but vibrate about some mean position and this is known as vibration.

7.4.1. Vibrating Diatomic Molecule

7.4.1.1. Simple Harmonic Oscillator

(I) Obeys Hooke's law i.e., f = – kx where f – restoring force; k – force constant and x – distance from equilibrium position.

(ii) Energy of simple harmonic oscillator is E = (1/2) kx^2.

(iii) An elastic bond has an intrinsic vibrational frequency, dependent on mass of the system and force constant but is independent of the amount of distortion. The oscillation frequency is given the expression,

$$\omega_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}Hz \qquad (1)$$

- where μ-reduced mass of the system = m_1m_2/m_1+m_2

  c – velocity of light (cms^{-1})

- The vibrational energy is quantised and is obtained from Quantum Chemistry and has the expression,

$$E_v = \left(v+\frac{1}{2}\right)h\omega_{osc} \quad \text{Joules} \quad (v = 0,1,2,.....) \qquad (2)$$

$$\varepsilon_v = \frac{E_v}{hc} = \left(v+\frac{1}{2}\right)\bar{\omega}_{osc} \quad c\text{m}^{-1} \qquad (3)$$

- The lowest vibrational energy for v = 0 is

$$E_0 = \frac{1}{2}h\omega_{osc} \quad \text{Joules}$$

$$\varepsilon_0 = \frac{1}{2}\bar{\omega}_{osc} \quad c\text{m}^{-1} \qquad (4)$$

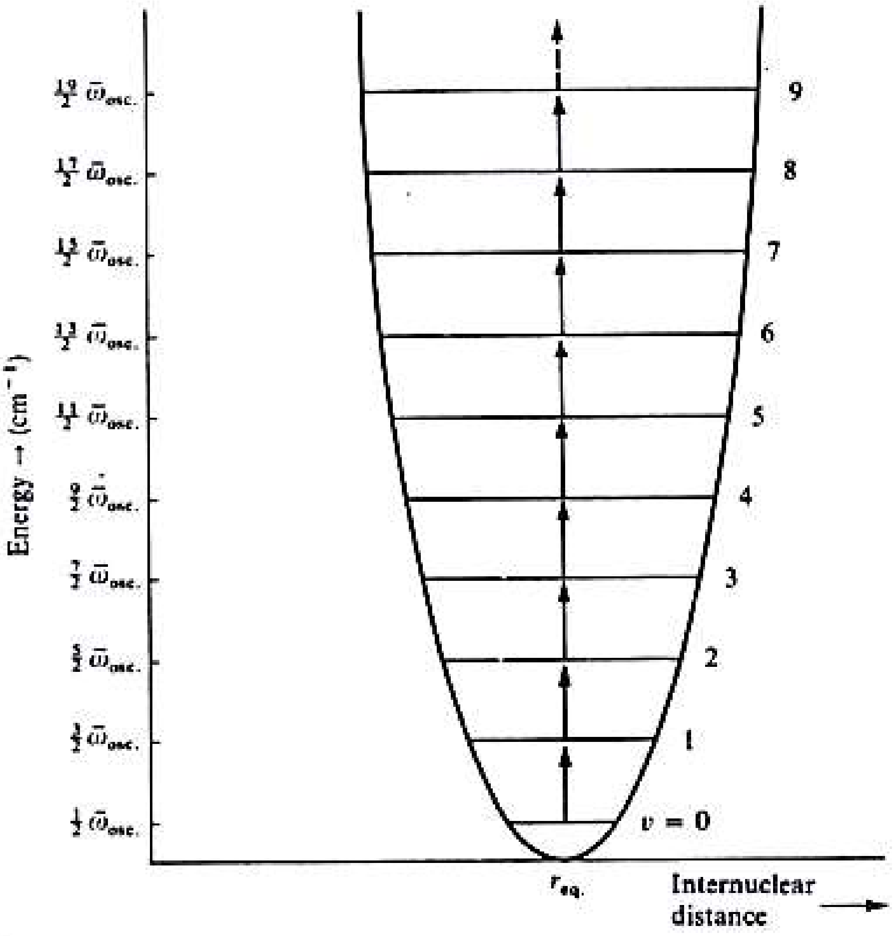
- Equ. (4), implies that a diatomic molecule can never have zero vibrational energy or the atoms can never be completely at rest relative to each other. This energy is called as zero point energy. The zero point energy depends on the classical vibration frequency and hence on the strength of the chemical bond and the atomic masses.

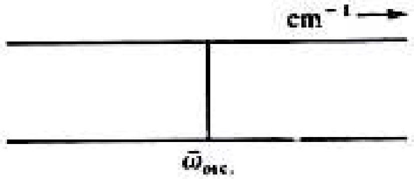
7.4.1.1.1. Selection Rule

(i) Vibrational energy changes will only give rise to an observable spectrum if the vibration can interact with radiation (i.e.,) if the vibration involves a change in the dipole moment of the molecule. Thus, vibrational spectra will be observable only in heteronuclear diatomic molecules since homonuclear molecule has no dipole moment.

(ii) The change in vibrational quantum number should be unity

$\Delta v = \pm 1$





- Applying this selection rule,

$$\varepsilon_{v+1\rightarrow v} = \left(v+1+\frac{1}{2}\right)\bar{\omega}_{osc} - \left(v+\frac{1}{2}\right)\bar{\omega}_{osc}$$

$$\varepsilon_{v+1\rightarrow v} = \bar{\omega}_{osc} \qquad \text{cm}^{-1}$$

- The difference between energy levels expressed in cm^{-1} gives directly the wavenumber of the spectral lines absorbed or emitte(d)

$$\bar{v}_{spectroscopic} = \varepsilon = \bar{\omega}_{osc} \qquad \text{cm}^{-1}$$

- Which means that the vibrating molecule will absorb energy only from radiation with which it can coherently interact and this must be radiation of its own oscillation frequency.

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UNIT-8 (ORGANIC CHEMISTRY)

TYPES OF REACTIONS, ELECTRON DISPLACEMENT METHODS & NOMENCLATURE OF ORGANIC COMPOUNDS

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(ii) Introduction of reduction and oxidation reactions

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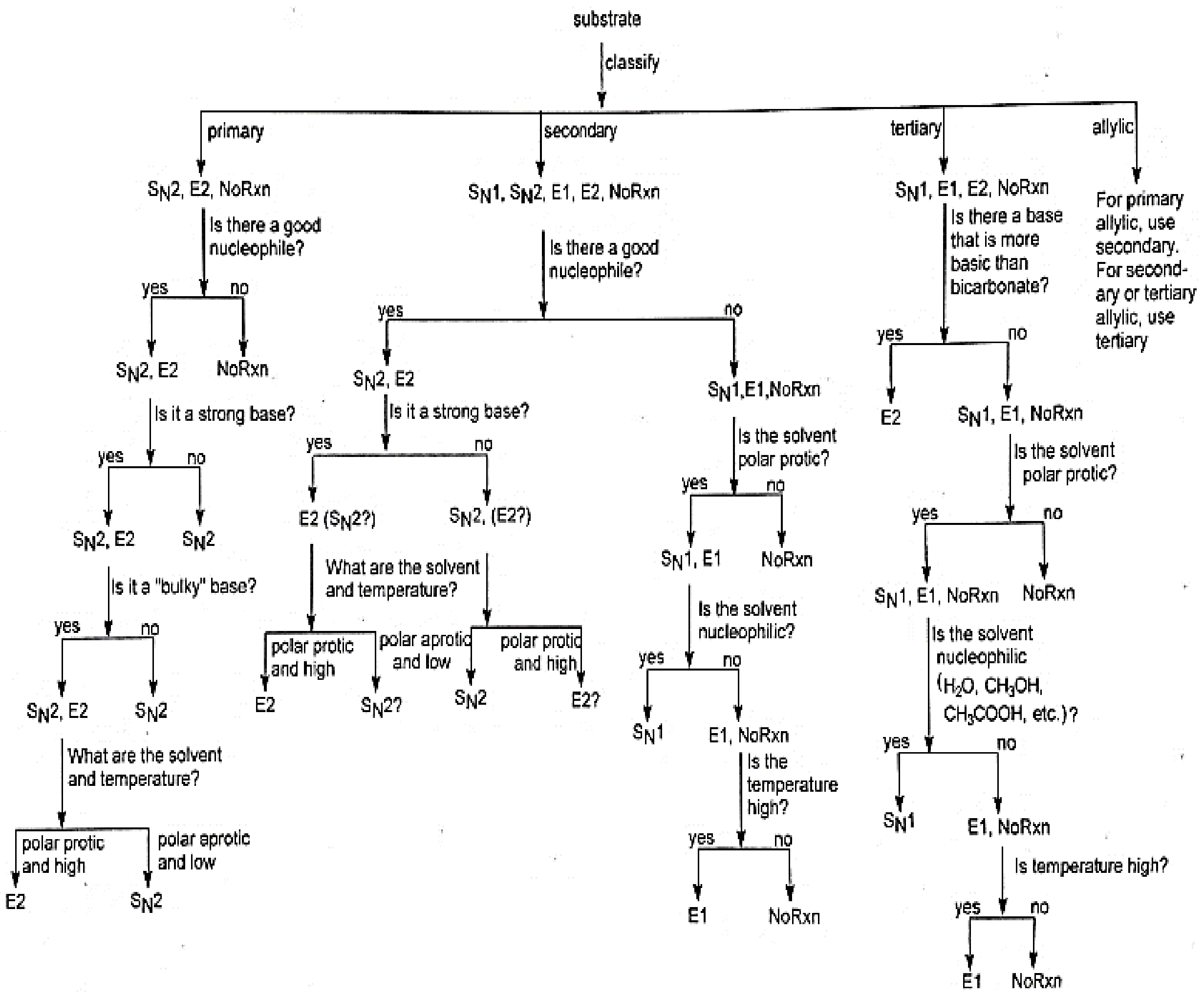
ORGANIC CHEMISTRY - UNIT 8

8.1. TYPES OF ORGANIC REACTIONS

8.1. Introduction and Types of Reactions:



Types of Organic Reactions

- It is convenient to classify the numerous reactions of the various classes of organic compound into four types,

- Substitution reactions,
- Addition reaction,
- Elimination reactions,
- Rearrangement reactions,

Or

1. Substitution Reaction

2. Elimination Reactions - E_1, E_2 & E_1cb

3. Addition Reactions –

(i) Electrophilic

(ii) Nucleophilic

(iii) Free radical

4. Rearrangements

1. Substitution Reactions:

- Replacement of an atom or group of the substrate by any other atom or group is known as substitution reactions.

Examples:

Leaving group *substituting or attacking group*

$$\downarrow\downarrow$$

$$\underset{\text{Ethyl bromide}}{CH_3-CH_2-Br} + NaOH \rightarrow \underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH} + NaBr$$

(Bromine atom is replaced by hydroxyl group)

Types of substitution reactions:

- On the basis of the nature of attacking species substitution reactions are classified into following three categories,

(1) Nucleophilic substitution reactions S_N1, S_N2 & S_Ni

(2) Electrophilic substitution reactions

(3) Free radical substitution reactions

(1) Nucleophilic Substitution Reactions:

(i) Many substitution reactions, especially at the saturated carbon atom in aliphatic compounds such as alkyl halides, are brought about by nucleophilic reagents or nucleophiles.

$$R - X \quad + \quad OH^{\ominus} \rightarrow R - OH + X^{\ominus}$$

Substrate nucleophile Leaving group

Such substitution reactions are called nucleophilic substitution reactions, i.e., SN reactions (S stands for substitution and N for nucleophile).

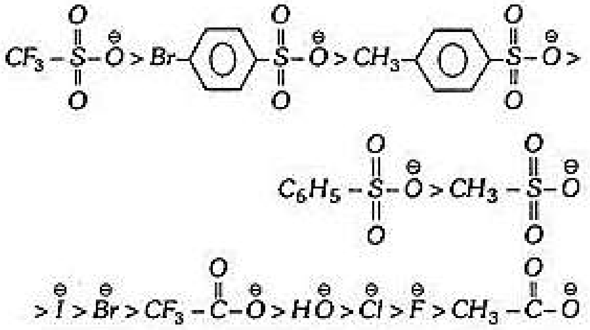
(ii) The weaker the basicity of a group of the substrate, the better is its leaving ability.

$$\text{leaving power of the group} \propto \frac{1}{\text{Basicity of the group}}$$

Example;

$$\underset{\text{Decreasing acidity}}{\underline{HI > HBr > HCl > HF}} \quad \underset{\text{Increasing basicity} \Rightarrow \text{Decreasing leaving ability}}{\underline{I\Theta > Br\Theta > HCl\Theta > HF\Theta}}$$

(iii) The leaving power of some nucleophilic groups are given below in decreasing order,



(iv) In these reactions leaving group of the substrate is replaced by another nucleophile. If reagent is neutral then leaving group is replaced by negative part of the reagent. Negative part of the reagent is always nucleophilic in character.

$$R - L \xrightarrow{\overset{+\delta}{E} - \overset{-\delta}{Nu}} R - Nu + \overset{\Theta}{L} \Big| R - L + \overset{\Theta}{Nu} \longrightarrow Nu + \overset{\Theta}{L} \Big|$$

Exercise Questions: I

1. Organic compounds are broadly classified as ________

A) Open chain compounds and acyclic compounds

B) Open chain compounds and linear chain compounds

C) Cyclic compounds and alicyclic compounds

D) alicyclic compounds and acyclic compounds

2. Aliphatic compound is the other name for ________

A) Acyclic compounds B) Alicyclic compounds

C) Ring compounds D) Closed chain compounds

3. Which among the following is not an example of Acyclic compound?

A) Acetaldehyde B) Ethane C) Cyclopropane D) Isobutane

4. Which among the following is not an example of alicyclic compound?

A) Cyclohexane B) Cyclohexene C) Tetrahydrofuran D) Acetic acid

5. Which among the following is not an aromatic compound (in specific)?

A) Naphthalene B) Aniline C) Pyridine D) Tropolone

6. Find the odd one among the following.

A) Alicyclic compounds B) Heterogeneous compounds

C) Branched chain compounds D) Aromatic compounds

7. Identify the odd one among the following.

A) Indene B) Anthracene C) o,m,p-xylene D) Azulene

8. Organic compounds can be classified even based upon the function groups. Identify the one which is not a functional group?

A) Isocyanide B) Isocyano C) Carboxyl D) Carbonyl

9. Which among the following is not a class of organic compound?

A) Carbonyl compound B) Nitro compound

C) Amides D) Electro compounds

10. Which among these is not associated with aliphatic compounds?

A) They contain $(4n+2)$ pi electrons

B) Contain straight chain compounds

C) Contain branched chain compounds

D) Has appropriate number of H-atoms and functional groups

8.1.1. Aliphatic Nucleophilic Substitution Reactions:

- When a substitution reaction is brought about by a nucleophile the reaction is termed as (SN) Nucleophilic substitution reaction.

S – Substitution N – Nucleophilic

- Nucleophilic substitution reactions are more common in aliphatic systems.

E.g. Hydrolysis of alkyl halides by aq. Alkali to form alcohols.

$$R-X+OH \longrightarrow R-OH+X^{-}$$

- Every Nucleophilic substitution reaction has three components
  - (i) Substrate
  - (ii) Nucleophile
  - (iii) Solvent
- **The substrate has two parts**
  - (i) Alkyl group (R)
  - (ii) Leaving group (L)
- Nucleophile may be either negatively charged (or) neutral species
- Substrate may be either positively charged (or) neutral species

The four Possibilities Are:

(i) $OH^- + CH_3 - Br \longrightarrow CH_3OH + Br^-$

(ii) $NH_3 + CH_3 - Br \longrightarrow CH_3 - NH_2$

(iii) $Cl^- + CH_3 - OH_2 \longrightarrow CH_3Cl + H_2O$

(iv)) $H_2S + RN\left(CH_3\right)_3 \longrightarrow H_2S - R + \left(CH_3\right)_3 N \longrightarrow H + HSR$

Nucleophilic Substitution Reaction may take place by Two Mechanisms:

(i) Unimolecular Nucleophilic substitution reaction $\left(\mathbf{SN}^1\right)$

(ii) Bimolecular Nucleophilic substitution reaction $\left(\mathbf{SN}^2\right)$

- The mechanism of Nucleophilic substitution reaction proceeds by Unimolecular (or) Bimolecular can be determined by kinetic studies.
- If the rate of the reaction is proportional to the concentration of the alkyl halide alone & independent of base then the reaction is unimolecular nucleophilic substitution reaction $\left(SN^1\right)$
- If the rate of the reaction is proportional to the concentration of the alkyl halide & also base then the reaction is bimolecular nucleophilic substitution reaction $\left(SN^2\right)$
- Rate $\alpha \left[RX\right]$ – Unimolecular $\left(SN^1\right)$
- Rate $\alpha \left[RX\right] \left[OH^-\right]$ – Bimolecular $\left(SN^2\right)$
- Bimolecular nucleophilic substitution reaction $\left(SN^1\right)$:

- The bimolecular mechanism is one process
- **E.g.** Reaction between methyl bromide aq.NaOH to form methanol

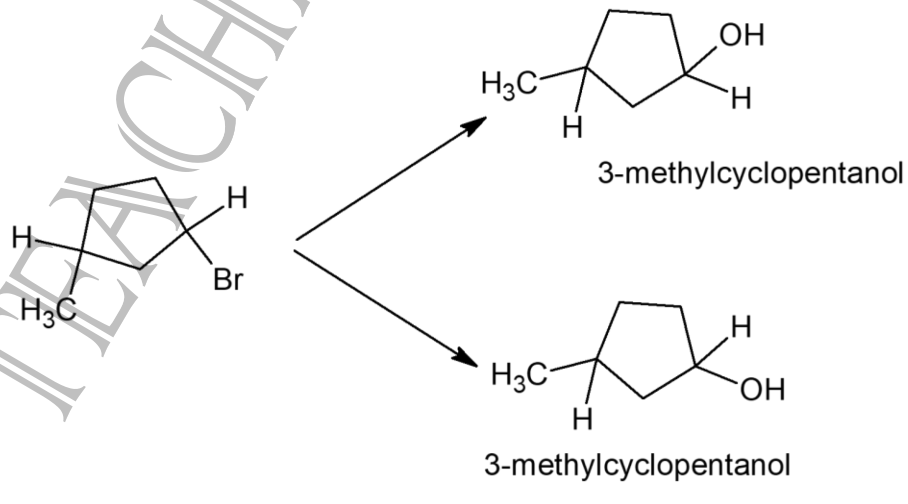
$$OH^- + CH_3Br \longrightarrow CH_3OH \ + \ Br^-$$

- The OH$^-$ ions attacks or colloids the carbon of methyl bromide from the side opposite to that of bromine due to steric strain & electrostatic repulsion.
- If collision has sufficient energy $C - OH$ bond forms & $C - Br$ bonds breaks. The bond making & breaking are simultaneously process. When the C-OH bond forms at the same time $C - Br$ bond breaks. This involves a transition state & here the carbon atom appears as pentavalent.
- Before OH^- the nucleophile attack the methyl bromide is in a tetrahedral shape. In the transition state the pentavalent is in planar structure here the OH^- & Br^- are present as for possible and the three hydrogen's in the carbon atom lie in a single plane at a bond angle of 120.when the leaving group Br- eliminated the OH^- nucleophile attached to the carbon atom and converted into alcohol which again converted into tetrahedral structure.
- But in the product inversion of configuration is obtained. The inversion of configuration is due to that nucleophile OH^- attacks the carbon atom to the opposite (or) back side of the leaving group. Hence there is inversion in configuration.
- The one step process of SN^2 mechanism is confirmed by the energy profile diagram.

Stereochemistry of SN^2 Reaction:

- In SN^2 reaction the nucleophile always attacks the carbon atom from the opposite leaving group. This is confirmed by the following stereochemistry reaction,

E.g. Hydrolysis of 3-methyl cyclo pentyl bromide by aq. NaOH solution gives trans- alcohol & not cis-alcohol.



- In SN_2 reaction the alkyl halide reactivity is in the order

$$CH_3Br > CH_3CH_2Br > CH_3CHCH_3Br > (CH_3)_3Br$$

Unimolecular Nucleophilic Substitution Reaction (SN^1):

- The Unimolecular mechanism is two step processes.

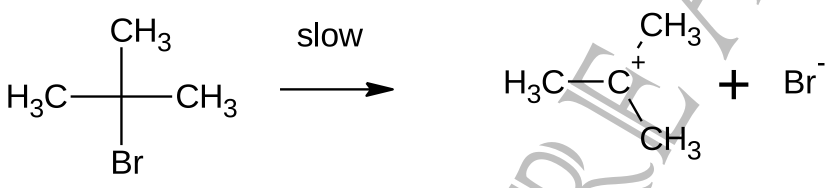
Example

- Hydrolysis of tertiary butyl bromide to give tertiary butyl alcohol.

$$(CH_3)_3CBr + OH^- \longrightarrow (CH_3)_3\,COH + Br^-$$

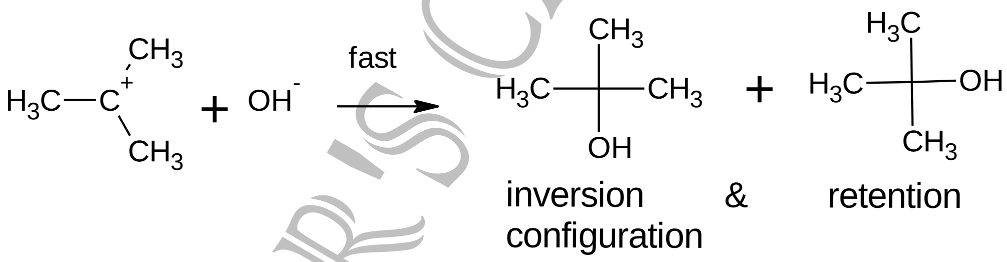
Step – I

- The first step is the ionization of tertiary butyl bromide to form tertiary butyl carbocation and Br- ion. This is slow step & is the rate determining step.



Step – II

- The nucleophile adds to the carbocation & forms alcohol.



- In SN^1 reaction the product is with inversion & retention in configuration.
- The two-step process of SN^1 reaction is confirmed by the energy profile diagram system.
- SN^1 reactions fail to proceed it the head of nor-bornyl systems. This is because SN^1 reaction requires carbocations which are planar. But bridge head carbon atoms cannot for planar carbocation.

Evidence for the Formation of Carbocation as Intermediate:

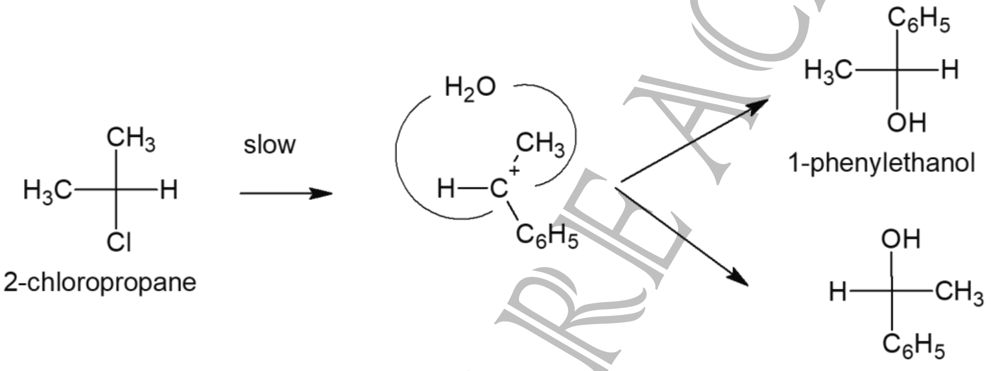
- When benzhydroxychloride is treated with tetra methyl ammonium fluoride in liq. SO_2 along with the expected product benzhydroxyfluoride, benzhydylchloride also obtained.

$$C_6CHClC_6H_5 + F^- \longrightarrow C_6CHCFC_6H_5 + C_6CHClC_6H_5$$

- The formation of two products benzhydroxyfluoride, benzhydylchloride is due to the formation of carbocation as intermediate. When benzhydylchloride cleaved into carbocation and chloride ion, to this added nucleophile fluoride ion or chloride ion can be joined so it results in to products.
- When no carbocation is formed only the expected product benzhydroxyfluoride is formed.
- Therefore, the formation of carbocation as intermediate is proved.

Stereochemistry of SN^1 Reactions:

- When 1 chloro1 phenyl ethane is treated with H_2O two products ethanol and (+) 1 phenyl ethanol were obtained.



- The first step is the formation of carbocation intermediate and is the slow step. The tetrahedral compound into a planar carbocation. Now the OH^- nucleophile attacks the carbocation from both the sides & results in retention & inversion configuration. During OH^- nuclephilic attacking the planar carbocation is again converted into tetrahedral structure.

Mixed SN^1 & SN^2 Mechanisms:

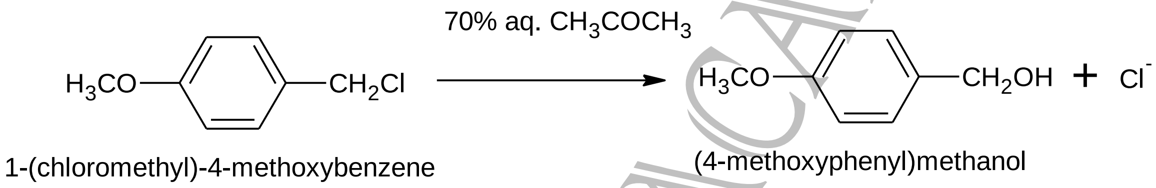
- These are some reactions which proceed with the mechanism in between SN^1& SN^2. This is called borderline mechanism.
- One theory holds that intermediate mechanism behavior is caused by a mechanism that is neither pure SN^2 but some in-between type.
- According to 2nd theory borderline behavior caused by simultaneous operation of both SN^1& SN^2 mechanisms. According to sneen all SN^1& SN^2 can be accommodated by one basic mechanism. The substrate first ionizes to an intermediate ion pair which is then converted into products.

$$RX \overset{K_1}{\rightleftarrows} R + X^- \overset{K_2}{\rightleftarrows} Products$$

- In SN^1 mechanism the formation of i
- on-pair is the rate determining step.
- In SN^2 mechanism the destruction of ion-pair is the rate determining step.
- Borderline behavior is found were the rate of formation and destruction of the ion-pair are of the same order of magnitude.

E.g. 4

- methoxy benzyl chlorides in 70% aq. acetone hydrolysis occur and converted into 4methoxy benzyl alcohol by SN^1 mechanisms.



- When azide ions are added, along the alcohol 4 methoxy benzyl azide is formed as another product addition azide ion increase the rate of ionization but decreases the rate of hydrolysis.
- If more carbocation formed fewer only converted into alcohol and some other converted in to azide by SN^1 reaction.
- But the rate of ionization is always less than the total rate of reaction. So some azide must also formed by SN^2 mechanism.
- SN^1 & SN^2 mechanisms operating in the same flask simultaneously.

Internal (or) Intramolecular Nucleophilic Substitution Reaction:

- In this process part of leaving group attacks the substrate detaches itself from the rest of the leaving group

$$ROH + SOCl_2 \longrightarrow RSO_2Cl + HCl$$

Step I:

- The alkyl chlorosulfinate dissociates into ion-pair

$$RSO_2Cl \longrightarrow R^+ + {}^-OSOCl$$

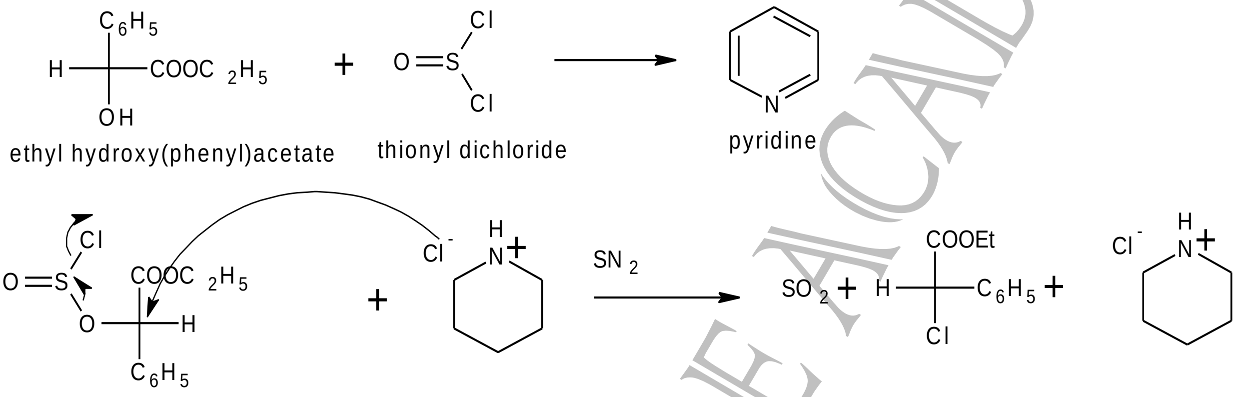
Step II

- Cl^- ion attacks the R^+ from the same side of the carbocation from which the leaving group departed and the product is formed with complete retention of configuration.

$$R^+ + {}^-OSOCl \longrightarrow R^-Cl + SO_2$$

Evidence:

- When pyridine is added to the reaction mixture of alcohol & thionyl chlorides. The product R-Cl is found with inversion of configuration.
- The pyridine co-ordinates with HCl produced during the formation of intermediate chlorosulfinate ester from ROH & $SOCl_2$.
- Inversion results because the pyridine reacts with ROSOCl to give $ROSON + C_6H_5$ then Cl^- freed in this process now attacks the alkyl group from the back side.



The Neighboring Group Participation:

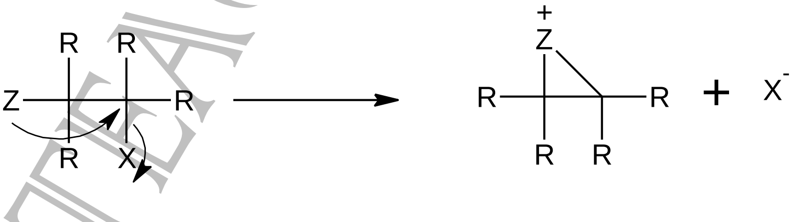
In some substrates

(i) The rate of reaction is greater expected and

(ii) The configuration of chiral carbon is retained & not inverted. This is due to neighboring group participation.

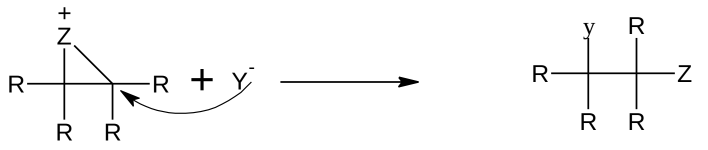
- In these cases there is a group with an unshared pair of electrons β to the leaving group. The mechanism operating in such cases is called the neighboring group mechanism. Here two SN^2 substitution reactions takes place, each is causing an inversion. So the net result is retention in configuration.
- The neighboring group participation mechanism involves two steps,

Step I



- Neighboring group acts as a nucleophile pushes out the leaving group but the neighboring group still attached to the molecule.

Step II



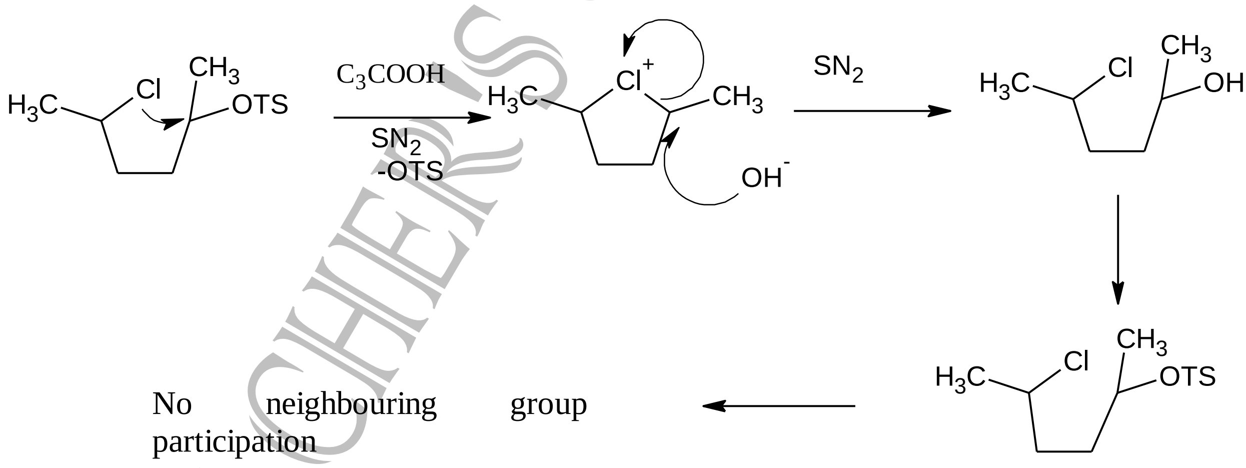
- The external nucleophile displaces the neighboring group by a backside attack.
- The nearby group increases the rate of the substitution reaction significantly
- The resulting increase in rate due to the neighboring group participation that would be expected is called anchemeric assistance.
- In Greek anchi - neighboring group mer: part

E.g. $OHCH_2CH_2Br$ rate of the reaction is faster than CH_3CH_2Br

- $PhSCH_2CH_2Cl$ hydrolysis occurs 600 times faster than $CH_3CH_2CH_2Cl$
- Some of the most important neighboring groups are COO- (but not COOH), COOR, COAr, $OCOR, OR, OH, O–, NH_2, NHR, NR_2, NHCOR, SH, SR, S^-, I, Br, \ \& \ Cl$
- The effectiveness of halogens is in the order
  I Br Cl

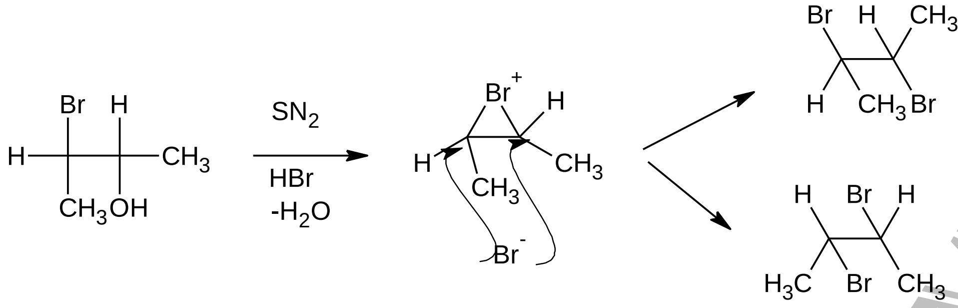
Chlorine acts as neighboring groups when only there is need for it.

E.g. 5-chloro-2-hexyl tosylate is solvolysed in trifluoroacetic acid with neighboring group's participation but not in CH_3COOH.



Halogen as Neighbouring Group:

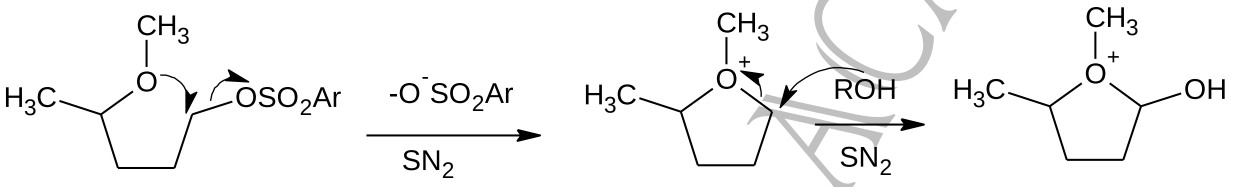
- The conversion of diastereisomeric 3-bromo-2-butanol to isomeric 2, 3 – dibromobutane is an example of neighbouring bromine participation in substitution reaction. If the reaction were normal SN^2 complete inversion would have occurred at the carbon undergoing substitution. If the reaction were racemisation would have occurred at the carbon undergoing substitution.

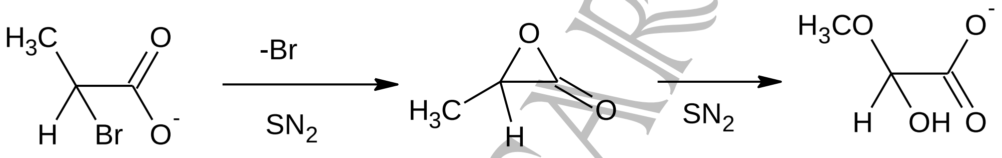


Oxygen as Neighbouring Group:

- Hydroxide group or methoxy group can assist substitution reactions through neighbouring group participation

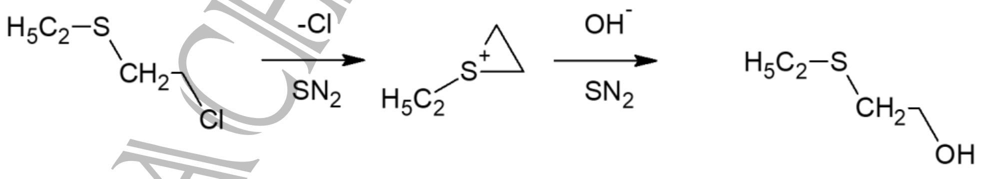
E.g. 4-methoxy alkyl sulfonate reacts with alcohols 4000 times faster than n-butyl sulfonate

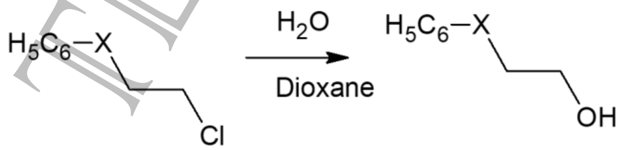




Sulphur as Neighboring Group:

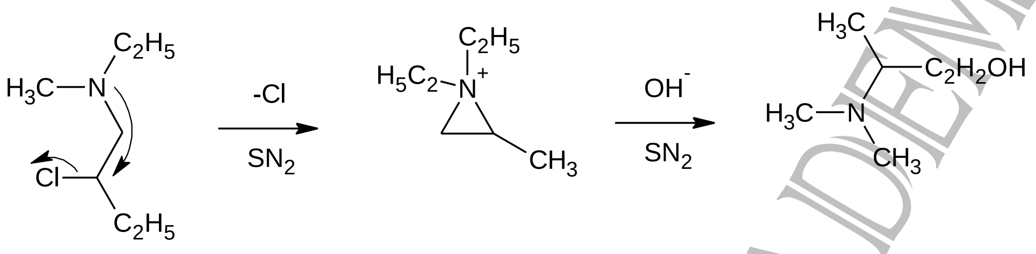
- Sulphur also takes part in neighbouring group participation sulphur atom is more powerful nucleophile than oxygen and its participation as a neighbouring group is stronger than oxygen.
- **E.g.** Hydrolysis of 2-chloro ethyl sulphide to corresponding alcohol. The rate of these reactions 103 times faster than the hydrolysis of 1-chlorohexane to 1-hexanol.





Nitrogen as a Neighbouring Group:

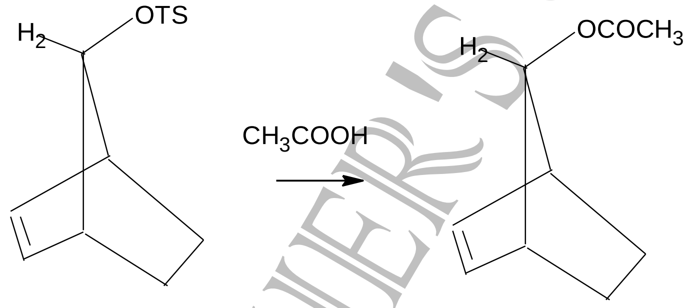
- Nitrogen with nonbonding electrons helps the substitution of hydroxyl group for halogen.
- But the substitution occurs with complete rearrangement.

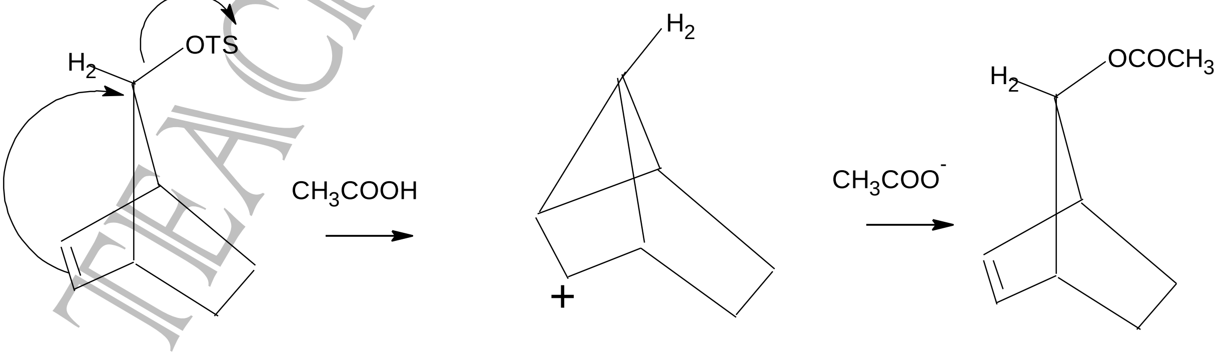


- N, N – dimethyl – 3- chlorobutamine on alkaline. Hydrolysis gives the cyclic intermediate aziridinium ion. Then the hydroxide ion attacks only at the less hindered carbon atom to give the rearranged product alcohol in which the amine group has migrated from carbon-1 to carbon-2.

Carbon – Carbon Double Bond (π - bond) as Neighbouring Group:

- Neighboring Carbon – carbon double bond in by cyclic tosylates increases the rate of acetolysis reaction and controls the stereochemistry of reaction.
- **E.g.** Acetolysis reaction tosylate of anti-7-hydroxybicyclohept-2-one in CH_3COOH proceeds 107 times faster than syn isomer and 1011 times faster than a saturated compound.





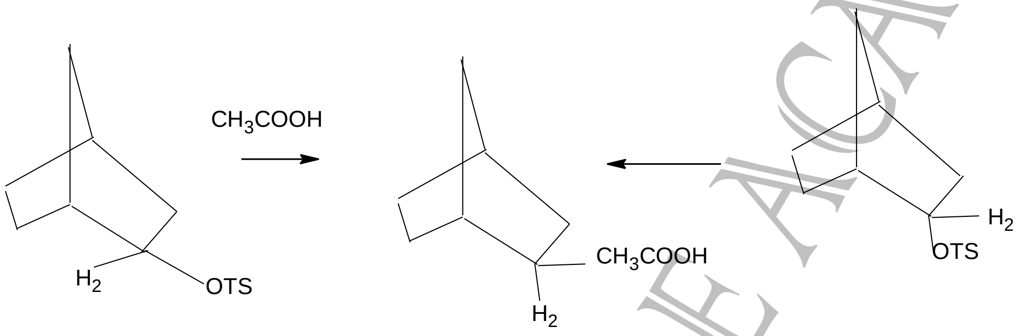
- The product formed is retention in configuration. The increase in rate is due to neighbouring double bonds helps in departing the tosylate group.

- When carbon - carbon double bond is anti to the tosylate the double bond helps in eliminating the leaving group in a intramoleccular SN^2 reaction & give classical carbonium ion. The opening of the resulting carbocation gives the anti-acetate & is alsoSN^2 reaction. The anti tosylate has the leaving group in favourable position for backside attack on the carbon having the leaving group.

Single Bond (σ bond) as Neighbouring Group [Non - Classical Carbocation]

- Even C-C bond electrons can helps in the ionisation of nearby leaving group.

E.g. Solvolysis reaction of diastereomeric exo& endo - 2 - norbornyltosylate in CH_3COOH both gives only exo - 2 - norbornyltosylate.



The exo - 2 - norbornyltosylate reacts 350 times faster than the endo - 2 - norbornyltosylate

Mechanism:

- In exo - isomer carbon - carbon bond helps in the expulsion of a leaving group and an intermediate bridged ion is formed. This bridged ion is called Non - classical carbocation.

Note:

- Non - classical carbocation are cyclic bridged ions and possess a three centre bond in which three atoms share two electrons.

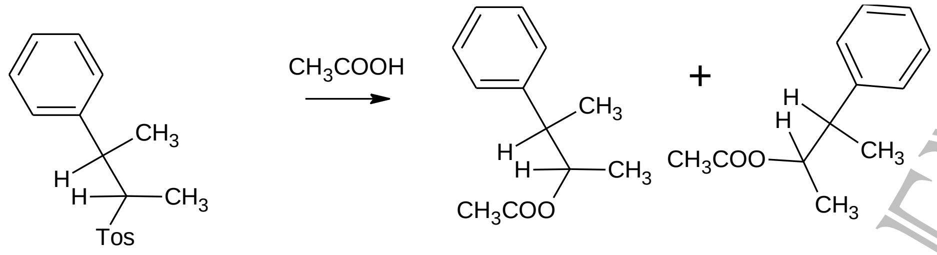
E.g: Norbornyl carbocation.

- This Non - classical carbocation is opened by CH_3COOH followed by deprotonation gives the exo - 2 - norbornyl acetate.
- The backside attack by sigma electrons on carbon having tosylate group helps to push out the tosylate and gives the bridged ion in single step. The geometry of endo – tosylate does not permit backside attack.
- Hence exo - tosylate reacts with neighbouring group participation. It reacts at the faster rate.

Aromatic groups as neighboring group:

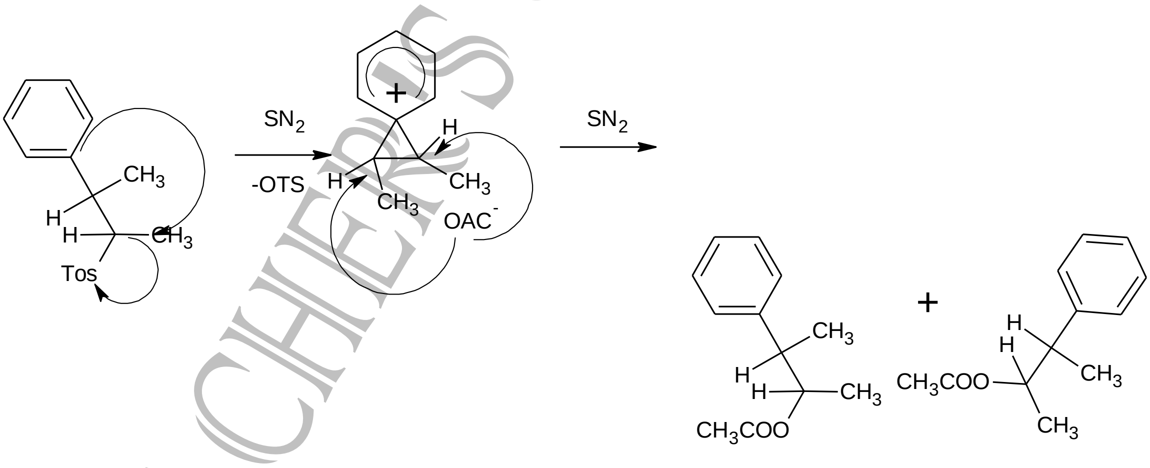
- The bi system of aromatic rings in the beta position also enters into neighboring group participation.

E.g. Threo 3 - phenyl - 2 - butyl tosylate reacts with CH_3COOH gives the racemic mixture of the corresponding 3 - phenyl - 2 - butyl acetate.



Threo-3-methyl-2-butyltosylate

- If the reaction follows SN^2 mechanism inversion of configuration occurs (threotosylate could give erythro acetate). If the reaction follows SN^1 mechanism it results in two different optically active products (mixture of threo&erythro acetates are formed).
- But cram observed that the optically active threotosylates gives threo acetates.
- This can be explained on the basis of the formation of bridged carbocation intermediate. i.e. phenonium ion.
- The bi system of the aromatic ring acts as a internal nucleophile & displaces tosylate by an intramolecular SN^2 mechanism. The resulting is phenonium ion is opened by the nucleophile CH_3COOH through intermolecular SN^1 reaction.
- Since there are two possible sites or attack of CH_3COOH thus the pair of enantiomers is obtained.



Nucleophilic substitution at an Allylic Carbon - Allylic Rearrangement:

- Allylic substrates undergo nucleophilic substitution rapidly accompanied by an allylic rearrangement. When allylic substrates are treated with nucleophile under SN^1 conditions two products were obtained.
- The formation of two products is due to the resonance hybrid of allylic type carbocation

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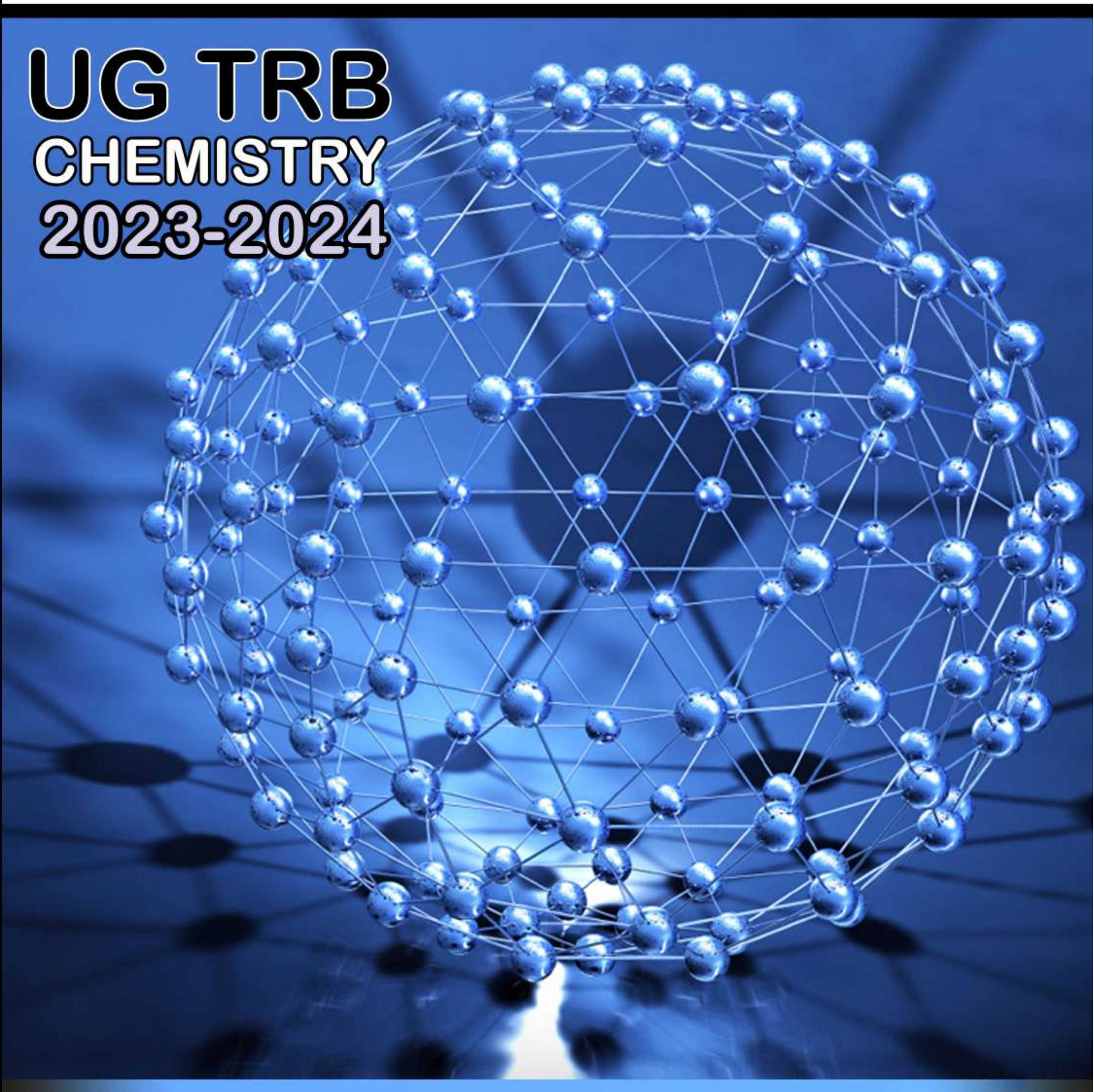

UG TRB
CHEMISTRY
2023-2024

UNIT-9
NATURE OF BONDING & STEREOCHEMISTRY

Your Success is Our Goal….

INDEX

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UG TRB – CHEMISTRY – 2023-24

ORGANIC CHEMISTRY - UNIT 9

A) NATURE OF BONDING

9.1. Introduction

- Since the ancient time ‘s people were aware of vegetation, animals and living beings. The basic concept of Organic Chemistry is based on the above ideas. The vegetation, animals and living beings are nothing but organic origin. Every item after burning is converted in to –Carbon and truly speaking Organic Chemistry can be called as **Carbon Chemistry**. The beautiful lady, handsome man and healthy plants and animals are known to be healthy carbon contents. The carbon comes from various sources, like vegetables, plants, animals etc. The human beings consume all types of vegetables and animal products.

- What are these products? How they are formed, is also a chemical phenomenon. The plants give various types of plant hormones, vitamins, terpenes, anthocyanin and flavones, various fatty acids, essential oils, medicinal and aromatic compounds, fibers etc. Here the Carbon-to-Carbon linkages give these above compounds. The Carbon may be linked by single bond (C-(C) or by double, triple or multiple bonds. Plants manufacture above compounds in presence of sunlight, water and of course minerals from earth. The linkages in **Carbon Chemistry** are called bonding and the bonding is responsible for various organic products. To describe the various aspects of this unit in studying the growth and development of organic products and to appraise growth, the identification, analysis and development of various products are with their structural mechanism.

- Chemical bonds are the attractive forces that hold atoms together in the form of compounds. They are formed when electrons are shared between two atoms. There are 3 types of bonds, covalent bonds, polar covalent bonds and ionic bonds. The simplest example of bonding can be demonstrated by the H_2 molecule.

- In 1939 American chemist Linus Pauling issued his textbook The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry.
- There are four major types of chemical bonds in chemistry, which includes, Ionic bond, Covalent bond, Metallic bond, and Hydrogen bond.
- Chemical Bonding refers to the formation of a chemical bond between two or more atoms, molecules, or ions to give rise to a chemical compound. These chemical bonds are what keep the atoms together in the resulting compound.
- **The attractive force which holds various constituents (atom, ions, etc.) together and stabilizes them by the overall loss of energy is known as chemical bonding.** Therefore, it can be understood that chemical compounds are reliant on the strength of the chemical bonds between its constituents, The stronger the bonding between the constituents, the more stable the resulting compound would be.
- The opposite also holds true, if the chemical bonding between the constituents is weak, the resulting compound would lack stability and would easily undergo another reaction to give a more stable chemical compound (containing stronger bonds). To find stability, the atoms try to lose their energy.
- Whenever matter interacts with another form of matter, a force is exerted on one by the other. When the forces are attractive in nature, the energy decreases. When the forces are repulsive in nature, the energy increases. The attractive force that binds two atoms together is known as the chemical bond.

9.1.1. Important Theories on Chemical Bonding

- Albrecht Kossel and Gilbert Lewis were the first to explain the formation of chemical bonds successfully in the year 1916. They explained chemical bonding on the basis of the inertness of noble gases.

9.1.1.1. Lewis Theory of Chemical Bonding

- An atom can be viewed as a positively charged 'Kernel' (the nucleus plus the inner electrons) and the outer shell.
- The outer shell can accommodate a maximum of eight electrons only.
- The eight electrons present in the outer shell occupy the corners of a cube which surround the 'Kernel'.
- The atoms having octet configuration, i.e., 8 electrons in the outermost shell, thus symbolize a stable configuration.

- Atoms can achieve this stable configuration by forming chemical bonds with other atoms. This chemical bond can be formed either by gaining (or) losing an electron(s) $\left(NaCl,\ MgCl_2\right)$ (or) in some cases due to the sharing of an electron.
- Only the electrons present in the outer shell, also known as the valence electrons take part in the formation of chemical bonds. Gilbert Lewis used specific notations better known as Lewis symbols to represent these valence electrons.
- Generally, the valency of an element is either equal to the number of dots in the corresponding Lewis symbol (or) 8 minus the number of dots (or valence electrons).
- Lewis symbols for lithium (1 electron), oxygen (6 electrons), neon (8 electrons) is given below in the Figure 1.
- 

Figure 1: Representation of electrons in Lithium, Oxygen and Neon

- Here, the number of dots that surround the respective symbol represents the number of valence electrons in that atom.

9.1.1.2. Kossel's Theory of Chemical Bonding

- Noble gases separate the highly electronegative halogens and the highly electropositive alkali metals.
- Halogens can form negatively charged ions by gaining an electron. Whereas alkali metals can form positively charged ions by losing an electron.
- These negatively charged ions and positively charged ions have a noble gas configuration that is 8 electrons in the outermost shell. The general electronic configuration of noble gases (except helium) is given by ns^2np^6.
- As unlike charges attract each other these unlike charged particles are held together by a strong force of electrostatic attraction existing between them. For example, $MgCl_2$, the magnesium ion, and chlorine ions are held together by force of electrostatic attraction. This kind of chemical bonding existing between two unlike charged particles is known as an electrovalent bond.

Explanation of Kossel Lewis Approach

- In 1916 Kossel and Lewis succeeded in giving a successful explanation based upon the concept of an electronic configuration of noble gases about why atoms combine to form molecules. Atoms of noble gases have little (or) no tendency to combine with each other (or) with atoms of other elements. This means that these atoms must be having stable electronic configurations.

- Due to the stable configuration, the noble gas atoms neither have any tendency to gain (or) lose electrons and, therefore, their combining capacity (or) valency is zero. They are so inert that they even do not form diatomic molecules and exist as monoatomic gaseous atoms.

9.2. Nature of Bonding in Inorganic Molecules

- Kossel & Lewis (1916) gave the Electronic Theory of Bonding to explain the formation of bond S or union between atoms, based on Bohr‘s Atomic Model. Where atom consist of a central positively charged nucleus, with neutrons and protons, having unit mass and the nucleus surrounded by the electrons, if the desired number of electrons (usually on octet) is not present in the last orbit it can be obtained by combining or losing or sharing electrons among themselves. The saturated outer orbit results in inert gases, which entertain no chemical reaction.

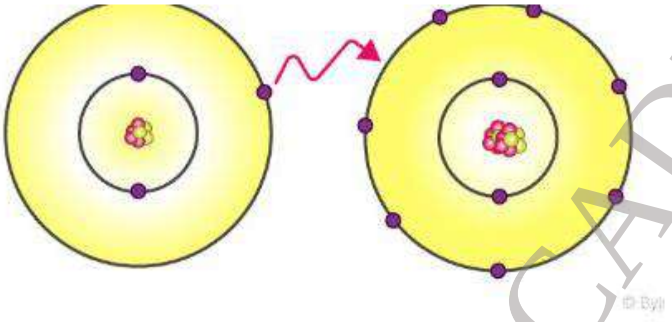
9.2.1. Types of Chemical Bonds:

- When substances participate in chemical bonding and yield compounds, the stability of the resulting compound can be gauged by the type of chemical bonds it contains.
- The type of chemical bonds formed vary in strength and properties. There are 4 primary types of chemical bonds which are formed by atoms (or) molecules to yield compounds. These types of chemical bonds include:
  - ✓ Ionic Bonds.
  - ✓ Covalent Bonds.
  - ✓ Hydrogen Bonds.
  - ✓ Polar Bonds.
- These types of bonds in chemical bonding are formed from the loss, gain, (or) sharing of electrons between two atoms/molecules.
- The different modes of bond formation arise as a result of different manners, in which electron distribution occurs between the combining atoms to attain the stable inert gas electronic configuration. The bonding thus established is of three types:
  - ✓ Ionic-bonding
  - ✓ Co-valentbonding
  - ✓ Co-ordinate-co-valent bonding or co-ordinate bonding.

I) Ionic Bonding

- ✓ Ionic bonding is a type of chemical bonding which involves a transfer of electrons from one atom (or) molecule to another. Here, an atom loses an electron which is in turn gained by another atom. When such an electron transfer takes place, one of the atoms develops a negative charge and is now called the anion.

- ✓ The other atom develops a positive charge and is called the cation. The ionic bond gains strength from the difference in charge between the two atoms, i.e. the greater the charge disparity between the cation and the anion, the stronger the ionic bond is represented in the Figure 2.

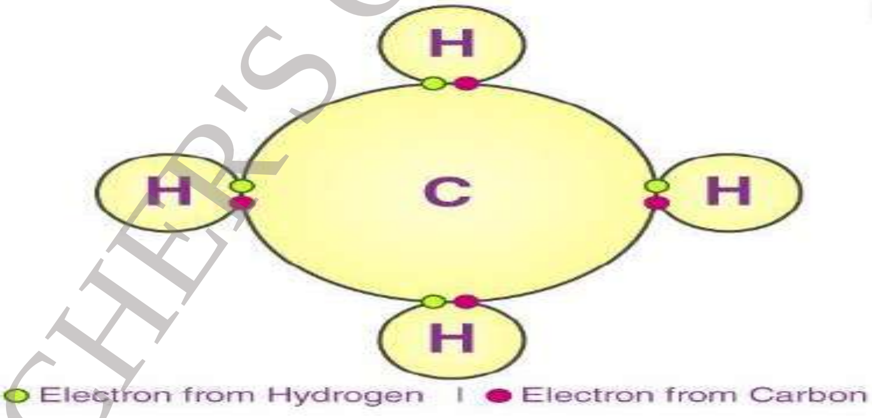


Types of Chemical Bonds – Ionic bonding

Figure 2: Indication of Ionic Bonding

II) Covalent Bonding

- ✓ A covalent bond indicates the sharing of electrons between atoms. Compounds that contain carbon (also called organic compounds) commonly exhibit this type of chemical bonding is shown in the Figure 3. The pair of electrons which are shared by the two atoms now extend around the nuclei of atoms, leading to the creation of a molecule.



Covalent Bonding

Figure 3: Representation of Covalent Bonding

III) Polar Covalent Bonding

- ✓ Covalent bonds can be either be Polar (or) Non-Polar in nature. In Polar Covalent chemical bonding, electrons are shared unequally since the more electronegative atom pulls the electron pair closer to itself and away from the less electronegative atom. Water is an example of such a polar molecule.

- ✓ A difference in charge arises in different areas of the atom due to the uneven spacing of the electrons between the atoms. One end of the molecule tends to be partially positively charged and the other end tends to be partially negatively charged.

IV) Hydrogen Bonding

- ✓ Compared to ionic and covalent bonding, Hydrogen bonding is a weaker form of chemical bonding. It is a type of polar covalent bonding between oxygen and hydrogen where in the hydrogen develops a partial positive charge. This implies that the electrons are pulled closer to the more electronegative oxygen atom.
- ✓ This creates a tendency for the hydrogen to be attracted towards the negative charges of any neighbouring atom. This type of chemical bonding is called a <u>hydrogen bond</u> and is responsible for many of the properties exhibited by water is shown in the Figure 4.

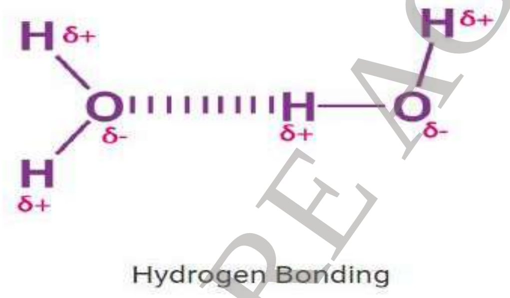


Figure 4: Illustration of Hydrogen Bonding

- ✓ The bond formed as a result of strong electrostatic forces of attraction between a positively and negatively charged species is called an <u>electrovalent (or) ionic bond</u>. The positively and negatively charged ions are aggregated in an ordered arrangement called the crystal lattice which is stabilized by the energy called the Lattice Enthalpy.

9.2.2 Conditions for the Formation of an Ionic Bond

- The low ionization energy of the atom forming the cation.
- High electron gain enthalpy of the atom forming the anion.
- High negative lattice enthalpy of the crystal formed.

Generally, the ionic bond is formed between a metal cation and non-metal anion.

9.2.3. The Method of Writing Lewis Structures

The following steps are adopted for writing the <u>Lewis's dot structures</u> or Lewis structures.

Step 1:

- ➢ Calculate the number of electrons required for drawing the structure by adding the valence electrons of the combining atoms. **For Example**, in methane, CH_4 molecule, there are 8 valence electrons (in which 4 belongs to carbon while other 4 to H atoms).

Step 2:

- Each negative charge i.e. for anions, we add an electron to the valence electrons and for each positive charge i.e. for cations we subtract one electron from the valence electrons.

Step 3:

- Using the chemical symbols of the combining atoms and constructing a skeletal structure of the compound, divide the total number of electrons as bonding shared pairs between the atoms in proportion to the total bonds.

Step 4:

- The central position in the molecule is occupied by the least electronegative atom. Hydrogen and fluorine generally occupy the terminal positions.

Step 5:

- After distributing the shared pairs of electrons for single bonds, the remaining electron pairs are used for multiple bonds or they constitute lone pairs.
- The basic requirement is that each bonded atom gets an octet of electrons.

Example 1: Lewis formula for carbon monoxide, CO

Step 1:

- Counting the total number of valence electrons of carbon and oxygen atoms: $C\left(2s^{2}2p^{2}\right) + O\left(2s^{2}2p^{4}\right)\ 4 + 6 = 10$ that is , $4(C) + 6(O) = 10$

Step 2:

- The skeletal structure of carbon monoxide is written as CO

Step 3:

- Drawing a single bond between C and O and completing octet on O, the remaining two electrons are lone pair on C is shown in the Figure 5.

Figure 5: Lewis's Structure of Carbon with Single Bond

Step 4:

- This does not complete the octet of carbon, and hence we have a triple bond is shown in the Figure 6.

Figure 6: Lewis's Structure of Carbon with Single Bond

Example 2: Lewis Structure of nitrite, NO_2^-

Step 1:

- Counting the total number of valence electrons of one nitrogen atom, two oxygen atoms and the additional one negative charge (equal to one electron) is shown in the Figure 7.
- Total Number of valence electrons is: $N\ (2s^2 2p^3)\ +\ 2O\ (2s^2 2p^4)\ +\ 1$ (negative charge)

  $\Rightarrow 5 + 2(6) + 1 = 18e^-$

Step 2:

- The skeletal structure of nitrite ion is written as $O - N - O$

Step 3:

- Drawing a single bond between nitrogen and each oxygen atom: $O - N - O$

Step 4:

- Complete the octets of atoms.

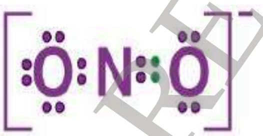


Figure 7: Representation of electrons inNitrite

- This structure does not complete octet on N if the remaining two electrons constitute of a lone pair on it. Therefore, It is a double bond between one N and one of the two O atoms. The Lewis structure is given in the Figure 8.

Figure 8: Lewis's structure of Nitrite

9.3. Bond Characteristics

9.3.1. Bond Length

- During chemical bonding, when the atoms come closer to each other, the attraction takes place between them and the potential energy of the system keeps on decreasing till a particular distance at which the potential energy is minimum. If the atoms come more closer, repulsion starts and again the potential energy of the system begins to increase.
- At equilibrium distance, the atoms keep on vibrating about their mean position. The equilibrium distance between the centres of the nuclei of the two bonded atoms is called its **Bond Length.**

- It is expressed in terms of an angstrom $\left(A^0\right)$ (or) picometer (pm). It is determined experimentally by x-ray diffraction (or) electron diffraction method (or) spectroscopic method. The bond length in chemical bonding is the sum of their ionic radii, in an ionic compound. In a covalent compound, it is the sum of their covalent radii. For a covalent molecule AB, the bond length is given by $d = r_a + r_b$

Factors Affecting the Bond length

- ✓ **Size of the atoms:** The bond length increases with increase in the size of the atom.
- ✓ $HI > HBr > HCl > HF$
- ✓ **The multiplicity of Bond:** The bond length decreases with an increase in bond order.
- ✓ **Type of hybridization:** A's' orbital is smaller in size, greater the 's' character, shorter is the bond length.

9.3.2. Bond Enthalpy

- When atoms come close together the energy is released due to the chemical bonding between them. The amount of energy required to break one mole of bonds of a type so as to separate the molecule into individual gaseous atoms is called **bond dissociation enthalpy (or) Bond enthalpy.** Bond enthalpy is usually expressed in $KJ\ mol^{-1.}$
- Greater is the bond dissociation enthalpy, greater is the bond strength. For diatomic molecules like $H_2, Cl_2, O_2, N_2, HCl, HBr, HI$ the bond enthalpies are equal to their dissociation enthalpy.
- In the case of polyatomic molecules, bond enthalpies are usually the average values, because the dissociation energy varies with each type of bond.
- In H_2O, first O-H bond enthalpy = 502 KJ/mol; Second bond enthalpy = 427 KJ/mol Average bond enthalpy = (502 + 427) / 2 = 464.5 KJ/mol.

9.3.2.1 Factors Affecting Bond Enthalpy in Chemical Bonding

I) Size of the Atom

Greater the size of the atom, greater is the bond length and less is the bond dissociation enthalpy i.e. less is the bond strength during chemical bonding.

II) Multiplicity of Bonds

Greater is the multiplicity of the bond, greater is the bond dissociation enthalpy.

III) Number of Lone Pair of Electrons Present

More the number of lone pair of electrons present on the bonded atoms, greater is the repulsion between the atoms and thus less is the bond dissociation enthalpy of the chemical bond.

9.3.3. Bond Angle

- A bond is formed by the overlap of atomic orbitals. The direction of overlap gives the direction of the bond. The angle between the lines representing the direction of the bond i.e. the orbitals containing the bonding electrons is called the **bond angle is shown in the Figure 9.**

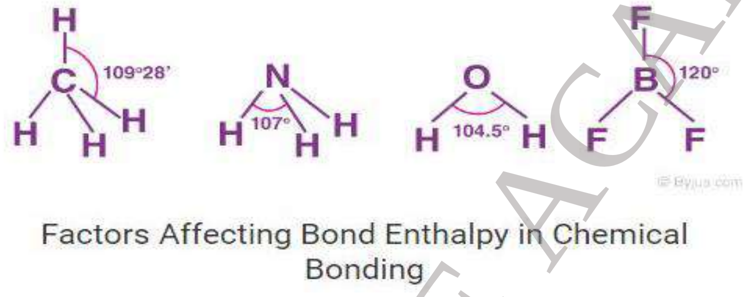


Figure 9: Illustration of Bond Angles of Various Elements

9.4 Bond Order

- In Lewis representation, the number of bonds present between two atoms is called the **Bond Order**. Greater the bond order, greater is the stability of the bond during chemical bonding i.e. greater is the bond enthalpy. Greater the bond order, shorter is the bond length.

9.4.1. Resonance in Chemical Bonding

- There are molecules and ions for which drawing a single Lewis structure is not possible. For example, we can write two structures of O_3 is shown in the **Figure 10.**

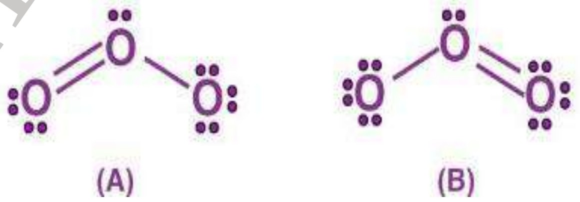


Figure 10: Illustration of Resonance in Ozone

- In (A) the oxygen-oxygen bond on the left is a double bond and the oxygen-oxygen bond on the right is a single bond. In B the situation is just the opposite. The experiment shows, however, that the two bonds are identical.
- Therefore, neither structure A nor B can be correct. One of the bonding pairs in ozone is spread over the region of all three atoms rather than localized on a particular oxygen-oxygen bond.

This delocalized bonding is a type of chemical bonding in which bonding pair of electrons are spread over a number of atoms rather than localized between two is represented in the **Figure 11.**

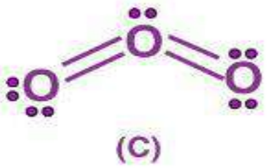


Figure 11: Representation of Localization in Ozone

- Structures (A) and (B) are called resonating or canonical structures and (C) is the resonance hybrid. This phenomenon is called resonance, a situation in which more than one canonical structure can be written for a species. The chemical activity of an atom is determined by the number of electrons in its valence shell. With the help of the concept of chemical bonding, one can define the structure of a compound and is used in many industries for manufacturing products in which the true structure cannot be written at all.

Some other Examples:

Resonance of CO_3^{2-} ion is illustrated in the Figure 12.

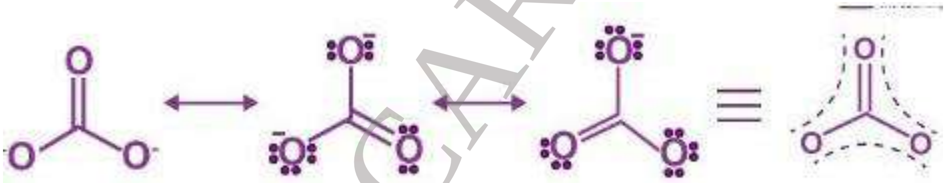
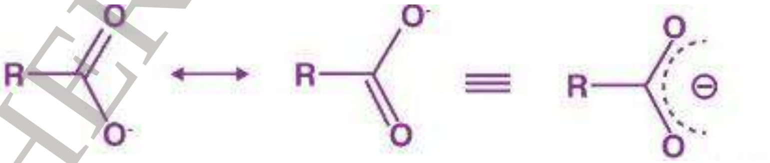


Figure 12: Illustration of resonance of CO_3^{2-} ion

Carbon-oxygen bond lengths in carboxylate ion are equal due to resonance.



Benzene

Vinyl Chloride

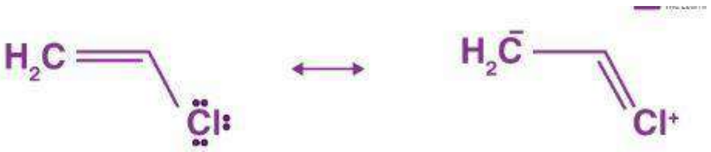


Figure 13: Resonance structure of Various molecules

The difference in the energies of the canonical forms and resonance hybrid is called resonance stabilization energy is shown in the **Figure 13**.

9.5. London Dispersion Forces

- Another form of chemical bonding is caused by London dispersion forces. These forces are weak in magnitude. These forces occur due to a temporary charge imbalance arising in an atom. This imbalance in the charge of the atom can induce dipoles on neighbouring atoms. For example, the temporary positive charge on one area of an atom can attract the neighbouring negative charge is shown in the **Figure 14.**

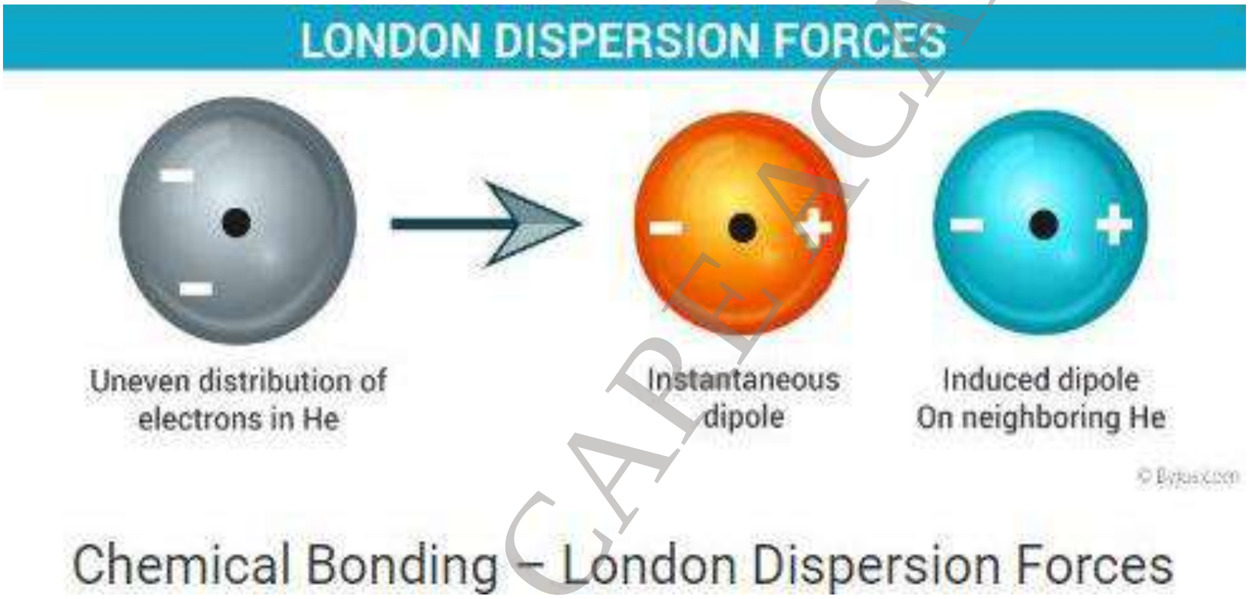


Figure 14: Illustration of London Dispersion Forces

- Atoms having eight electrons in their last orbit are stable and have no tendency to react. Atoms having less than eight electrons, then react with other atoms to get eight electrons in their outermost orbit, and become stable. Atoms having slightly excess than eight electrons may lose them, to atoms, which, are short of eight. Atoms that cannot either loss (or) gain, may share to get octet configuration. Molecules short of octet configuration even after the reaction, may accept lone pair of electrons present in other atoms (or) molecules.
- In metals, outer orbitals of atoms overlap and so the electrons present in them do not belong to any particular atom but flow over to all atoms as well and bind them all together (metallic bonding). Atoms that have to lose and gain electrons, becomes ions and are held together by the electrostatic forces of attraction (Ionic Bon(d). When atoms equally give and share electrons, the shared electrons become the unifying force between them (covalent bon(d). Electron-deficient and free lone pair containing molecules may again and satisfy the octet thirst of the electron-deficient atom. The shared electron bridges the electron-rich atom with electron-deficient atom (coordinate bon(d).

- Relatively similar energy sub-orbitals may merge and form a new set of the same number of orbitals, having the property of all the contributing orbitals in proportion to their numbers. These orbitals are hybridized orbitals. They are useful in explaining the similarity in bond length, bond angles, structure, shape and magnetic properties of molecules.
- sp^3 orbitals are formed from the s -subshell with uniform electron distribution around the nucleus and of p-subshell with distribution in the three vertical axis. Hybridized orbitals, hence have their electron distribution in three dimensions, as tetrahedral directions.
- In dsp^2 all the orbitals involved I hybridization have their electron distribution around the same plane. Hence, the hybridized orbitals also are in the same plane giving rise to square planar geometry.
- Oxygen atom shares two electrons, each with another oxygen atom to form the oxygen molecule. Oxygen molecule exhibits paramagnetic nature indicating unpaired electrons. A molecular orbital theory has been proposed to explain this. According to this theory, atoms lose their orbitals and rather form an equal number of orbitals covering the entire molecule and hence the name molecular orbital. Filling up of these orbitals in increasing energy order leaves unpaired electron explaining the paramagnetic behaviour of oxygen molecule.

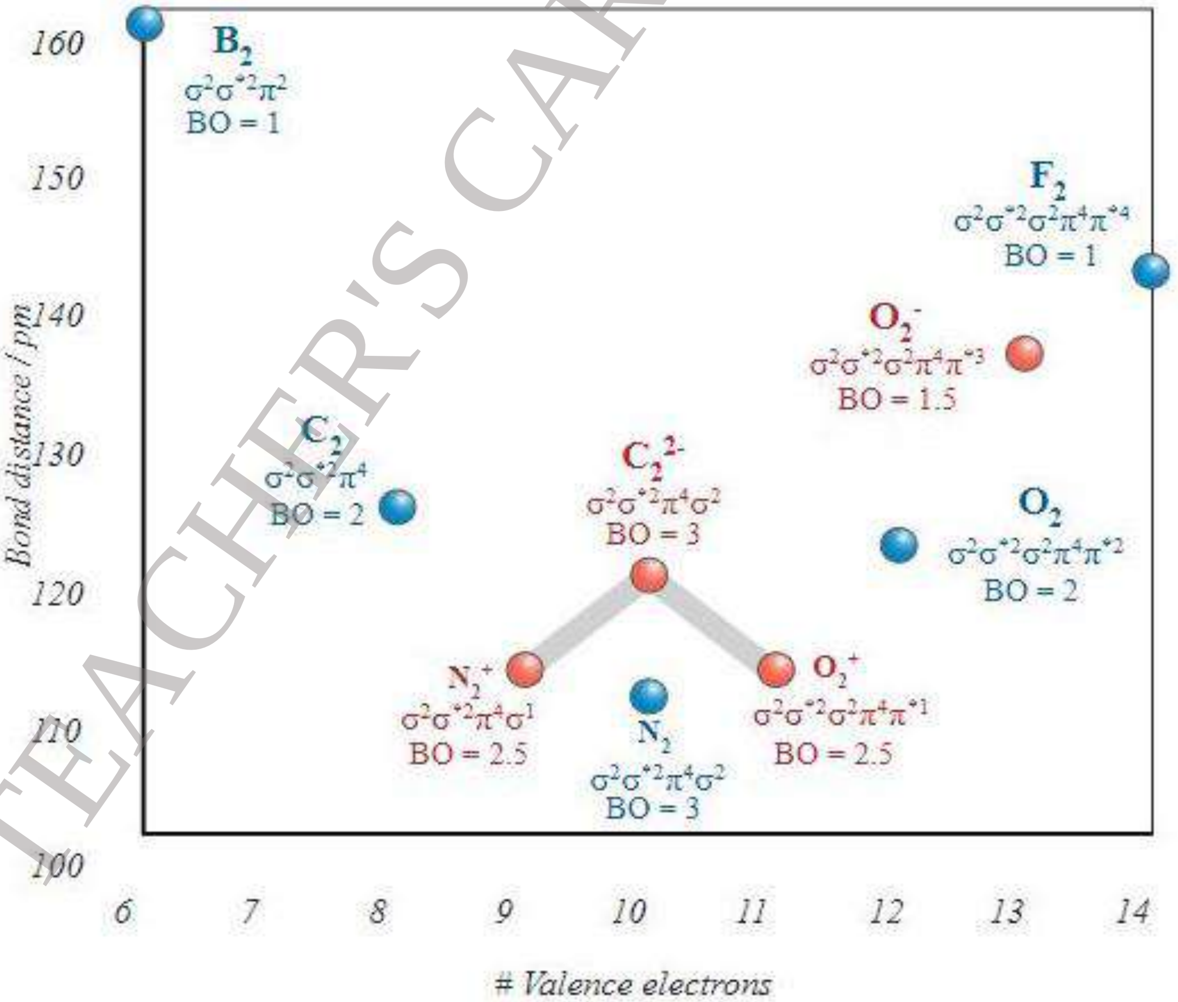


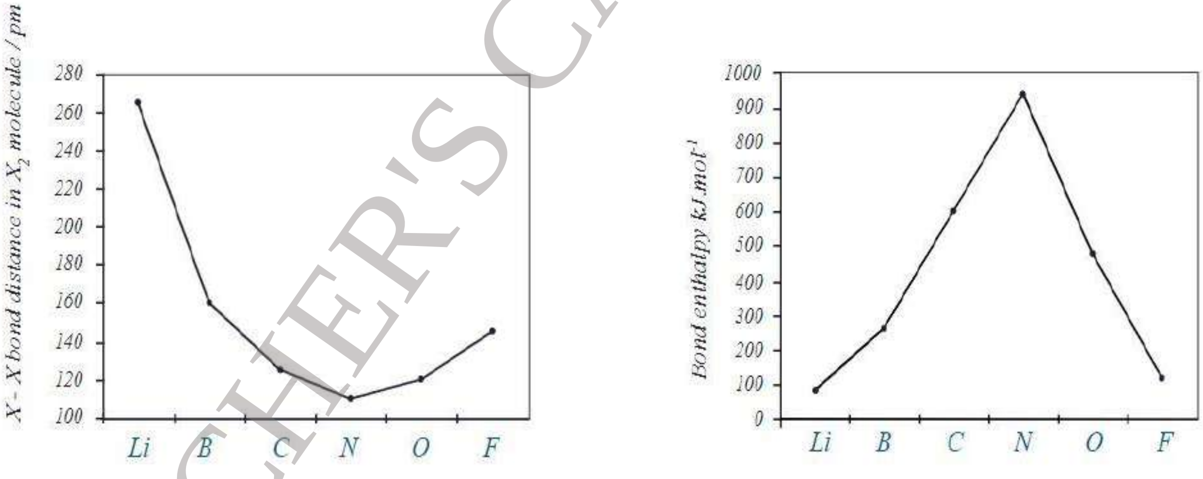
Figure 15: Bond Order of Various Molecules

- In general chemistry courses, students learn that covalent bonds can come as either single, double (or) triple bonds, which are identifies by their bond order. Both bond length and bond energy changes as the bond order increases and as the number of electrons shared between two atoms in a molecule increases, the bond order of a bond increases, the strength of the bond increases and the distance between nuclei decreases is shown in the Figure 15.

Table 1: Summary of various elements bond order, bond enthalpy, Bond length

Bond	Bond order	Bond Enthalpy (kJ/mol)	Bond Length ((A)
$C-C$	1	348	1.54
$C=C$	2	614	1.34
$C\equiv C$	3	839	1.20
$N-N$	1	163	1.47
$N=N$	2	418	1.24
$N\equiv N$	3	941	1.10

- The above trend can be observed in the first-row diatomic molecules. The bond order can be determined directly form the molecular orbital electron configurations. For diatomic, the occupations can correlate to bond length, bond energiesis shown in the Figure 16.



Plot of bond length (left) and bond energy (right) for first row diatomics (CC BY – NC; umit Kaya via Libretexts)

Figure 16: Illustration of Graph for first row diatomics

- It turns to a molecular orbital description of the bonding in O_2 It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. None of the other bonding models (e.g., Valence Bond theory (or) Lewis bonding) can predict the presence of two unpaired electrons in O_2 Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. It is actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches.

- The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus, the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a spin barrier.
- Organic compounds are covalent compounds According to the modern Valence Band Theory concept, a covalent bond is formed between two atoms if there is an overlapping of an atomic orbital of one atom with an atomic orbital of another atom. For an effective overlap, it is necessary that two atomic orbitals of the two different atoms must be half filled and approach each other in proper direction. The resultant orbital after overlapping is known as molecular orbital and has two electrons with oppositee spins. The effective over lapping is possible by two ways:

(i) **End to end overlapping:** This type of overlapping is possible betweens-s, s-p and p-p atomic orbitals. The molecular bond formed is termed as sigma bond.

(ii) **Sidewise or parallel or lateral overlapping:** Such overlapping is possible between p-p atomic orbitals. The molecular bond formed is termed as pi-bond. Sigma bond is stronger than bond. The electrons in the sigma bondare loosely held. The bond is easily broken and is more reactive than sigma bond. The amount of energy released during overlapping indicates the strength of the bond. Greater will be the strength of bond if higher energy is released during overlapping. Energy released during sigma bond formation is always more than the pi-bond because of greater over lapping in the former. The valency of the atom depends on the number of sigma bonds formed or sigma and pi bond formed.

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UNIT-10

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UG TRB – CHEMISTRY – 2023-24

ORGANIC CHEMISTRY - UNIT 10

A) MECHANISM IN AROMATIC SUBSTITUTION

10.1. Aromatic Electrophilic Substitution

- In aromatic compounds substitution may take place by electrophilic, nucleophilic or free radical mechanism. In this unit electrophilic substitution is discussed, there is a pi -electron cloud above and below the aromatic ring. These pi -electrons areloosely held as compared to sigma -electrons and are available to electrophiles. Thus, electrophilic substitutions are characteristic reactions of aromatic compounds. On the other hand, the electrons cloud above and below the plane of an aromatic ring shields the ring carbon from the attack of anucleophile. Electrophilic aromatic substitution reactions are organic reactions where in an electrophile replaces an atom which is attached to an aromatic ring. Commonly, these reactions involve the replacement of a hydrogen atom belonging to a benzene ring with an electrophile.
- Based on its structure and properties, what kinds of reactions should benzene undergo? Are any of its bonds particularly weak? Does ithave electron-rich or electron-deficient atoms?
    - Benzene has sixo electrons delocalized in six p orbitals that overlap above and below the plane of the ring. These loosely held o electrons make the benzene ring electron rich, and so it reacts with electrophiles.
    - Because benzene's six electrons satisfy Hückel'srule, benzene is especially stable. Reactions that keep the aromatic ring intact are therefore favored.
    - As a result, the characteristic reaction no of benzeneis electrophilic aromatic substitution—ahydrogenatom is replaced by anelectrophile is shown in the **Figure 1.**

Aromatic Electrophilic substitution

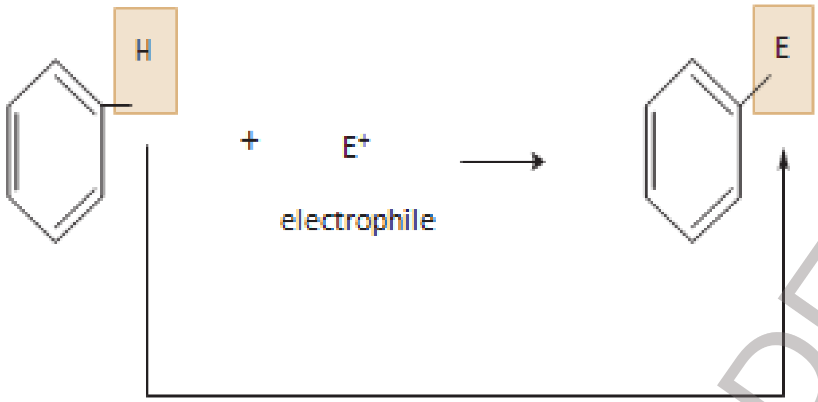


Figure 1: Schematic representation of Electrophilic Substitution in Aromatic ring

- Benzene does not undergo addition reactions like other unsaturated hydrocarbons, because addition would yield a product that is not aromatic. Substitution of hydrogen, on the other hand, keeps the aromatic ring intact is represented in **Figure 2.**

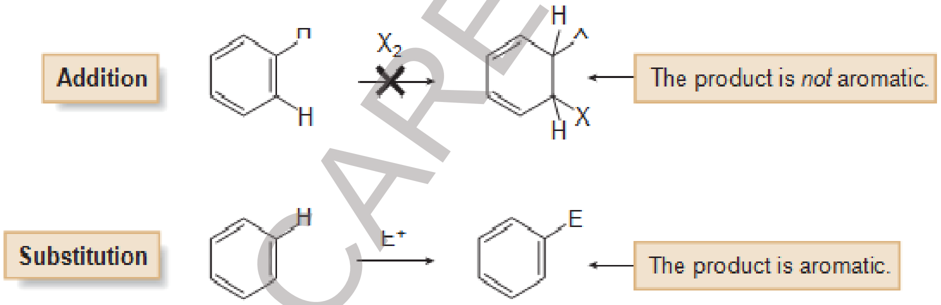


Figure 2: Representation of Addition and Substitution Reaction in aromatic ring

- The remarkable stability of the unsaturated hydrocarbon benzene has been discussed in an earlier section. The chemical reactivity of benzene contrasts with that of the alkenes in that substitution reactions occur in preference to addition reactions, as illustrated in the following **Figure 3.**

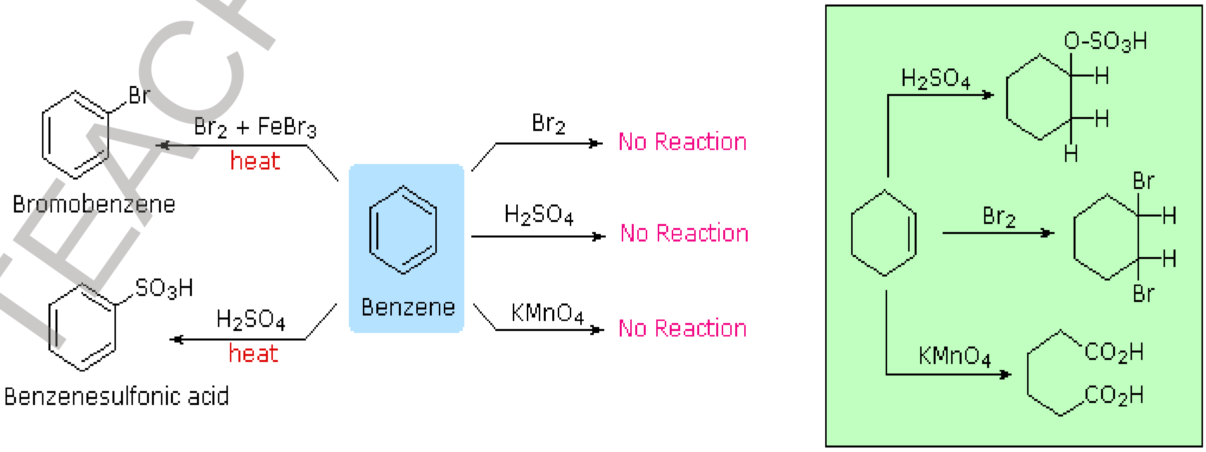
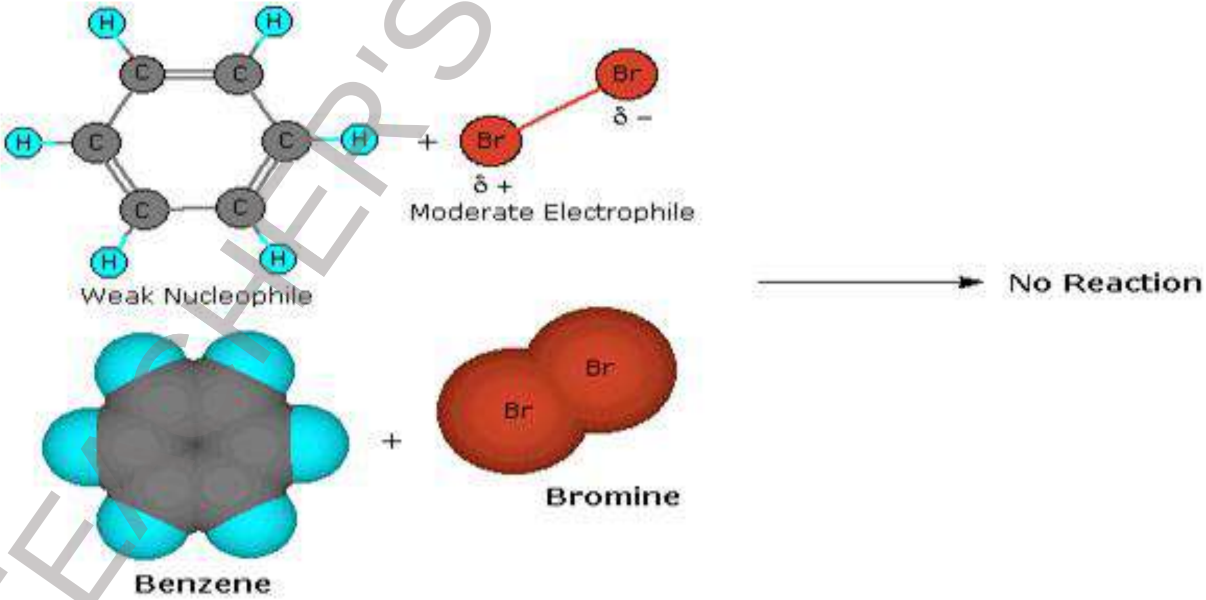


Figure 3: Illustration of addition and substitution reaction with Example

- A demonstration of bromine substitution and addition reactions is helpful at this point, and a virtual demonstration may be initiated. Many other substitution reactions of benzene have been observed, the five most useful are listed below (chlorination and bromination are the most common halogenation reactions). Since the reagents and conditions employed in these reactions are electrophilic, these reactions are commonly referred to as Electrophilic Aromatic Substitution. The catalysts and co-reagents serve to generate the strong electrophilic species needed to affect the initial step of the substitution. The specific electrophile believed to function in each type of reaction is listed in the right-hand column.
- Halogenation is an example of electrophilic aromatic substitution. In electrophilic aromatic substitutions, benzene is attacked by an electrophile which results in substitution of hydrogen. However, halogens are not electrophilic enough to break the aromaticity of benzenes, which require a catalyst to activate.

10.1.1. A Mechanism for Electrophilic Substitution Reactions of Benzene:

- A two-step mechanism has been proposed for these electrophilic substitution reactions. In the first, slow or rate-determining, step the electrophile forms a sigma-bond to the benzene ring, generating a positively charged benzenonium intermediate. In the second, fast step, a proton is removed from this intermediate, yielding a substituted benzene ring. The following four-part illustration shows this mechanism for the bromination reaction. Also, an animated diagram may be viewed in **Figure 4.**



- The bromine molecule is polarized so that one end is electrophillic and the other nucleophilic although the electrophillic end reacts easily with simple alkenes and dienes; it fails to react with the more stable and weaker electrophillic π - electron syatem of benzene.

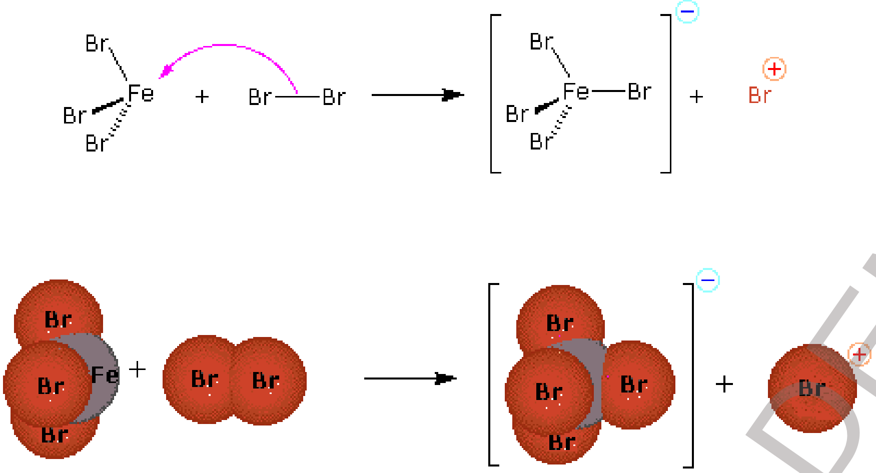


Figure 4: Representation of Bromination reaction

- Ferric bromide and other lewis acids enhance the electrophilic strength of bromine by forming a complex anion, in this case $FeBr_4^{\ominus}$. At the same time, this complexation creates the strongly electrophillic bromine cation, which reacts with nucleophiles.
- Preliminary step: Formation of the strongly electrophilic bromine cation: It is shown in the **Figure 5.**

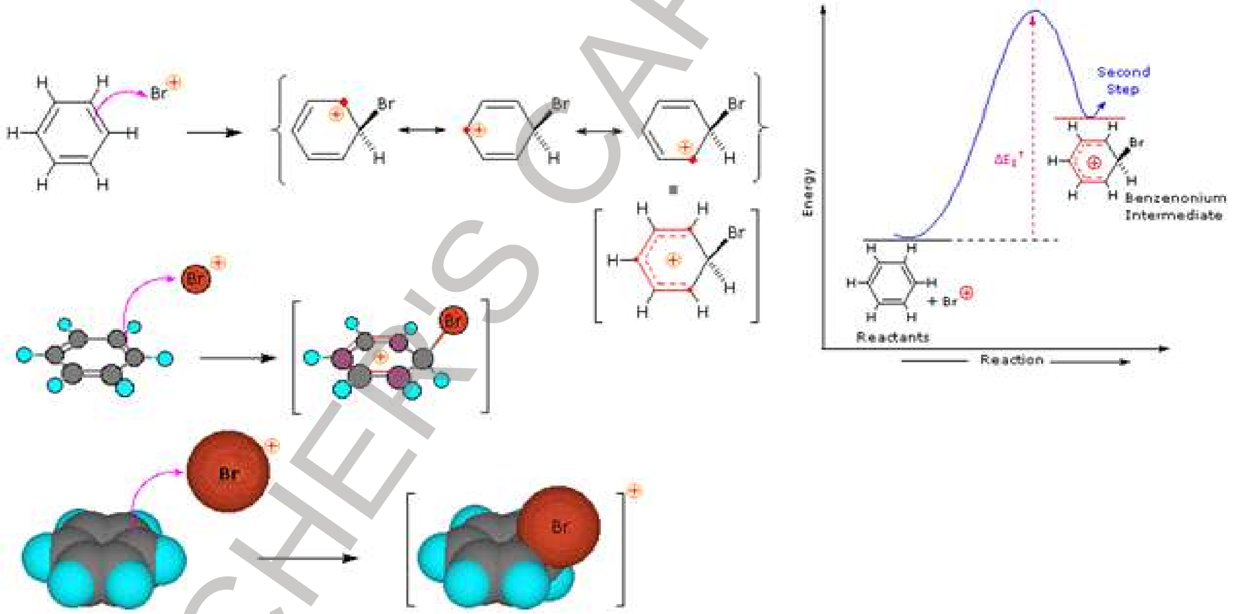


Figure 5: Indication of formation of the strongly electrophilic bromine cation

- The $\pi-$ electrons of the benzene ring are polarized by the electrophillic, and two electrons are diverted to form a $\pi-$bond to the bromine atom. The positive charge is there by relocated on the six- carbon ring, where it is confugated with the remaining double bonds. The resulting intermediates are a benzenonium cation. Since the aromatic character of benzence is lost the activation energy $\left(\Delta E_1^t\right)$ for this reaction is large. Note that the charge alternates so it greatest ortho and para to the location of the bromine attack.

Step 1: The electrophile forms a sigma-bond to the benzene ring, generating a positively charged **benzenonium intermediate formation is shown in Figure 6.**

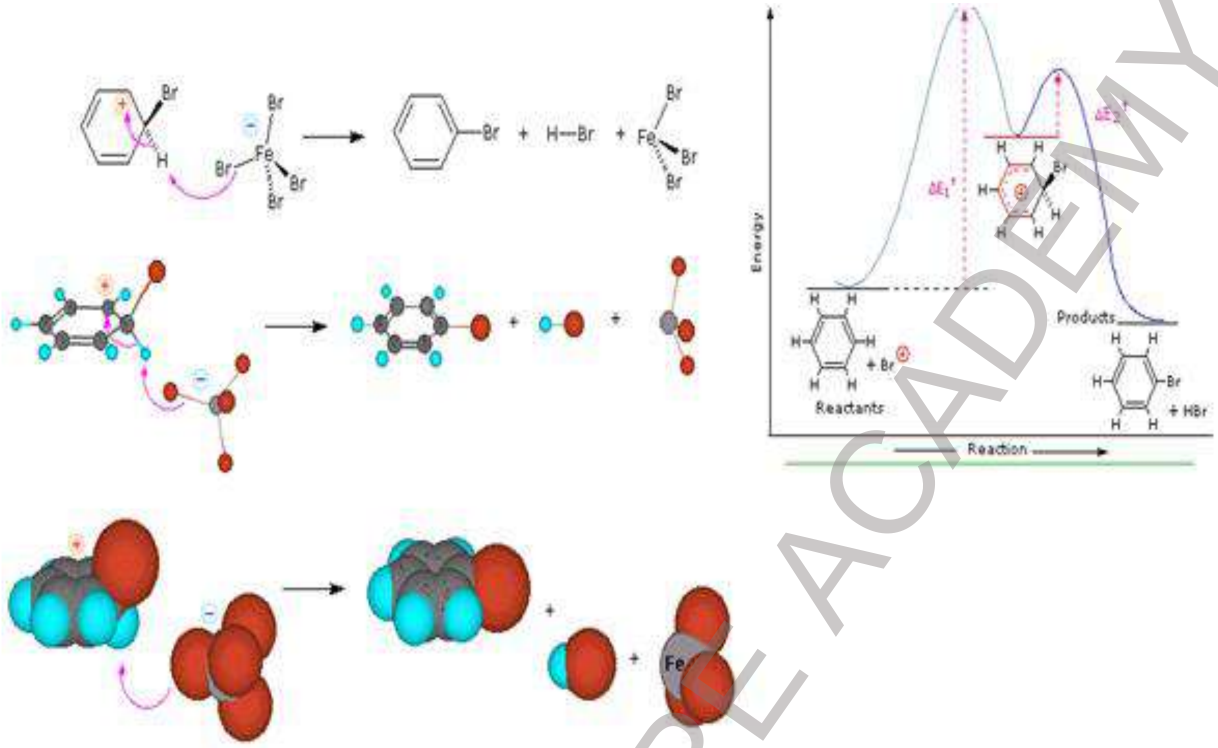


Figure 6: Illustration of formation of Intermediate in Step I

- In the second step of the bromination reaction, a base abstract the hydrogen proten bonded to the only sp^3 hybridized carbon atom in the ring. Any base will serve for this purpose, but the most likely candidate in this case is $Br^{\ominus}$, or its complex with ferric bromide $\left(FeBr_4^{\ominus}\right)$. The remaining electron pair immediately bonds to one of the adjacent positively charges carbons to reform the aromatic ring , which now bears a bromine substituent. Since the proton transfer gives a very stable product, its activation energy $\left(\Delta E_2^t\right)$ is small and the reaction is fast.
- This mechanism for electrophilic aromatic substitution should be considered in context with other mechanisms involving carbocation intermediates. These include SN_1 and E_1 reactions of alkyl halides, and Bronsted acid addition reactions of alkenes.
- To summarize, when carbocation intermediates are formed one can expect them to react further by one or more of the following modes:

1. The cation may bond to a nucleophile to give a substitution or addition product.
2. The cation may transfer a proton to a base, giving a double bond product.
3. The cation may rearrange to a more stable carbocation, and then react by mode at 1 or by 2.

- S_N1 and E_1 reactions are respective examples of the first two modes of reaction. The second step of alkene addition reactions proceeds by the first mode and any of these three reactions may exhibit molecular rearrangement if an initial unstable carbocation is formed. The carbocation intermediate in electrophilic aromatic substitution (the benzenonium ion) is stabilized by charge delocalization (resonance) so it is not subject to rearrangement. In principle it could react by either mode 1 or 2, but the energetic advantage of reforming an aromatic ring leads to exclusive reaction by mode 2 (*ie.* proton loss).

10.1.2. Substitution Reactions of Benzene Derivatives:

- When substituted benzene compounds undergo electrophilic substitution reactions of the kind discussed above, two related features must be considered:
- The first is the relative reactivity of the compound compared with benzene itself. Experiments have shown that substituents on a benzene ring can influence reactivity in a profound manner. For example, a hydroxy or methoxy substituent increases the rate of electrophilic substitution about ten thousand-fold, as illustrated by the case of anisole in the virtual demonstration (above). In contrast, a nitro substituent decreases the ring's reactivity by roughly a million. This activation or deactivation of the benzene ring toward electrophilic substitution may be correlated with the electron donating or electron withdrawing influence of the substituents, as measured by molecular dipole moments. In the following diagram we see that electron donating substituents (blue dipoles) activate the benzene ring toward electrophilic attack, and electron withdrawing substituents (red dipoles) deactivate the ring (make it less reactive to electrophilic attack) is shown in the **Figure 7.**

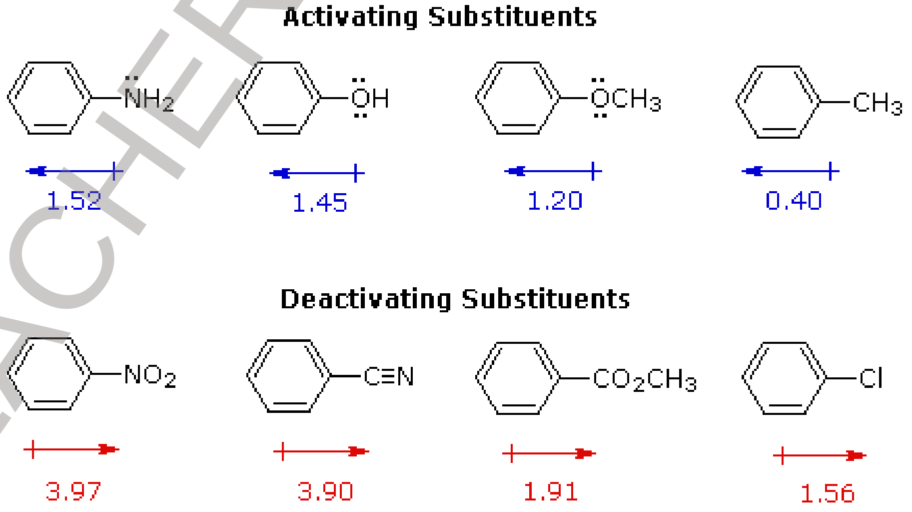


Figure 7: Indication of Various activating and Deactivating Substituents

- The influence a substituent exerts on the reactivity of a benzene ring may be explained by the interaction of two effects:

- The first is the inductive effect of the substituent. Most elements other than metals and carbon have a significantly greater electronegativity than hydrogen. Consequently, substituents in which nitrogen, oxygen and halogen atoms form sigma-bonds to the aromatic ring exert an inductive electron withdrawal, which deactivates the ring.
- The second effect is the result of conjugation of a substituent function with the aromatic ring. This conjugative interaction facilitates electron pair donation or withdrawal, to or from the benzene ring, in a manner different from the inductive shift. If the atom bonded to the ring has one or more non-bonding valence shell electron pairs, as do nitrogen, oxygen and the halogens, electrons may flow into the aromatic ring by p-π conjugation (resonance), as in the middle diagram. Finally, polar double and triple bonds conjugated with the benzene ring may withdraw electrons, as in the right-hand diagram. Note that in the resonance examples all the contributors are not shown. In both cases the charge distribution in the benzene ring is greatest at sites ortho and para to the substituent.
- In the case of the nitrogen and oxygen activating groups displayed in the top row of the previous diagram, electron donation by resonance dominates the inductive effect and these compounds show exceptional reactivity in electrophilic substitution reactions. Although halogen atoms have non-bonding valence electron pairs that participate in p-π conjugation, their strong inductive effect predominates, and compounds such as chlorobenzene are less reactive than benzene. The three examples on the left of the bottom row (in the same diagram) are examples of electron withdrawal by conjugation to polar double or triple bonds, and in these cases the inductive effect further enhances the deactivation of the benzene ring. Alkyl substituents such as methyl increase the nucleophilicity of aromatic rings in the same fashion as they act on double bonds is indicated in the **Figure 8.**

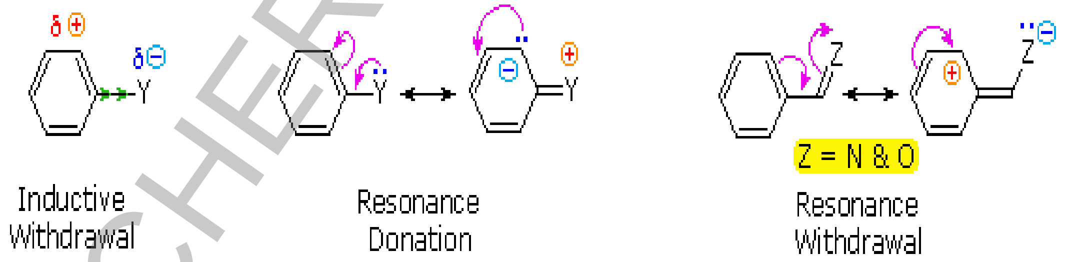


Figure 8: Representation of Resonance in electrophilic substitution

- The second factor that becomes important in reactions of substituted benzenes concerns the site at which electrophilic substitution occurs. Since a mono-substituted benzene ring has two equivalent ortho-sites, two equivalent meta-sites and a unique para-site, three possible constitutional isomers may be formed in such a substitution. If reaction occurs equally well at all available sites, the expected statistical mixture of isomeric products would be 40% ortho, 40% meta and 20% para. Again we find that the nature of the substituent influences this product ratio in a dramatic fashion. Bromination of methoxybenzene (anisole) is very fast and gives mainly the para-bromo isomer, accompanied by 10% of the ortho-isomer and only a trace of the meta-isomer. Bromination of nitrobenzene requires strong heating and produces the meta-bromo isomer as the chief product is shown in the **Figure 9.**

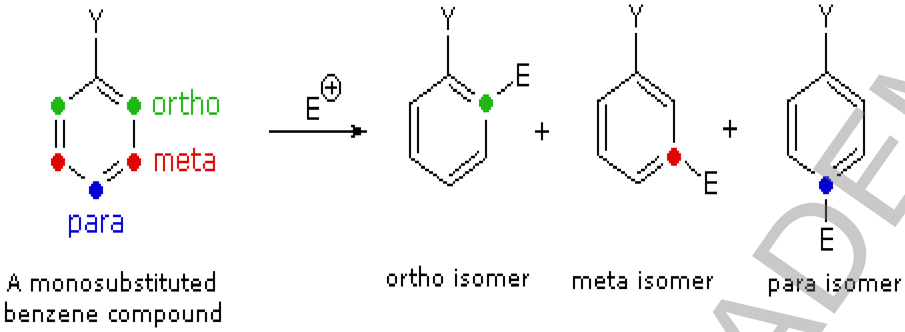


Figure 9: Schematic representation of Isomers

- Some additional examples of product isomer distribution in other electrophilic substitutions are given in the table below. It is important to note here that the reaction conditions for these substitution reactions are not the same, and must be adjusted to fit the reactivity of the reactant C_6H_5-Y. The high reactivity of anisole, for example, requires that the first two reactions be conducted under very mild conditions (low temperature and little or no catalyst). The nitrobenzene reactant in the third example is very unreactive, so rather harsh reaction conditions must be used to accomplish that reaction.
- Summary of formation of Isomers in percentage wise is listed in the **Table 1.**

Table 1: Summary of formation of Isomers in percentage wise

Y in C_6H_5-Y	**Reaction**	**% Ortho-product**	**% Meta - product**	**% para-product**
$-O-CH_3$	Nitration	30-40	0- 2	60-70
$-O-CH_3$	F-C Acylation	5-10	0- 5	90-95
$-NO_2$	Nitration	5- 8	90- 95	0-5
$-CH_3$	Nitration	55-65	1-5	35-45
$-CH_3$	Sulfonation	30-35	5- 10	60-65
$-CH_3$	F-C Acylation	10-15	2-8	85-90
$-Br$	Nitration	35- 45	0-4	55-65
$-Br$	Chlorination	40-45	5-10	50-60

- These observations, and many others like them, have led chemists to formulate an empirical classification of the various substituent groups commonly encountered in aromatic substitution reactions. Thus, substituents that activate the benzene ring toward electrophilic attack generally direct substitution to the ortho and para locations. With some exceptions, such as the halogens, deactivating substituents direct substitution to the meta location.

Orientation F_1 and reactivity effects of ring substituent's:

It is given in the figure 10

Activating substituents ortho & para – orientation	**Deactivating substituents meta – orientation**	**Deactivating substituents ortho & para – orientation**
$-O^{(-)}$ $-NH_2$	$-NO_2$ $-CO_2H$	$-F$
$-OH$ $-NR_2$	$-NR_3^{(+)}$ $-CO_2R$	$-Cl$
$-OR$ $-NHCOCH_3$	$-PR_3^{(+)}$ $-CHO$	$-Br$
$-OC_6H_5$ $-R$	$-SR_2^{(+)}$ $-COR$	$-I$
$-OCOCH_3$ $-C_6H_5$	$-SO_3H$ $-CN$	$-CH_2Cl$
	$-SO_2R$	$-CH=CHNO_2$

Figure 10: Indication of Orientation and Reactivity effects of Ring Substituents

- The information summarized in the above Figure 10 is very useful for rationalizing and predicting the course of aromatic substitution reactions, but in practice most chemists find it desirable to understand the underlying physical principles that contribute to this empirical classification. We have already analyzed the activating or deactivating properties of substituents in terms of inductive and resonance effects, and these same factors may be used to rationalize their influence on substitution orientation.

- The first thing to recognize is that the proportions of ortho, meta and para substitution in a given case reflect the relative rates of substitution at each of these sites. If we use the nitration of benzene as a reference, we can assign the rate of reaction at one of the carbons to be 1.0. Since there are six equivalent carbons in benzene, the total rate would be 6.0. If we examine the nitration of toluene, tert-butylbenzene, chlorobenzene and ethyl benzoate in the same manner, we can assign relative rates to the ortho, meta and para sites in each of these compounds. These relative rates are shown (colored re(d) in the following illustration and the total rate given below each structure reflects the 2 to 1 ratio of ortho and meta sites to the para position. The overall relative rates of reaction, referenced to benzene as 1.0, are calculated by dividing by six. Clearly, the alkyl substituents activate the benzene ring in the nitration reaction, and the chlorine and ester substituents deactivate the ring is represented in the **Figure 11.**

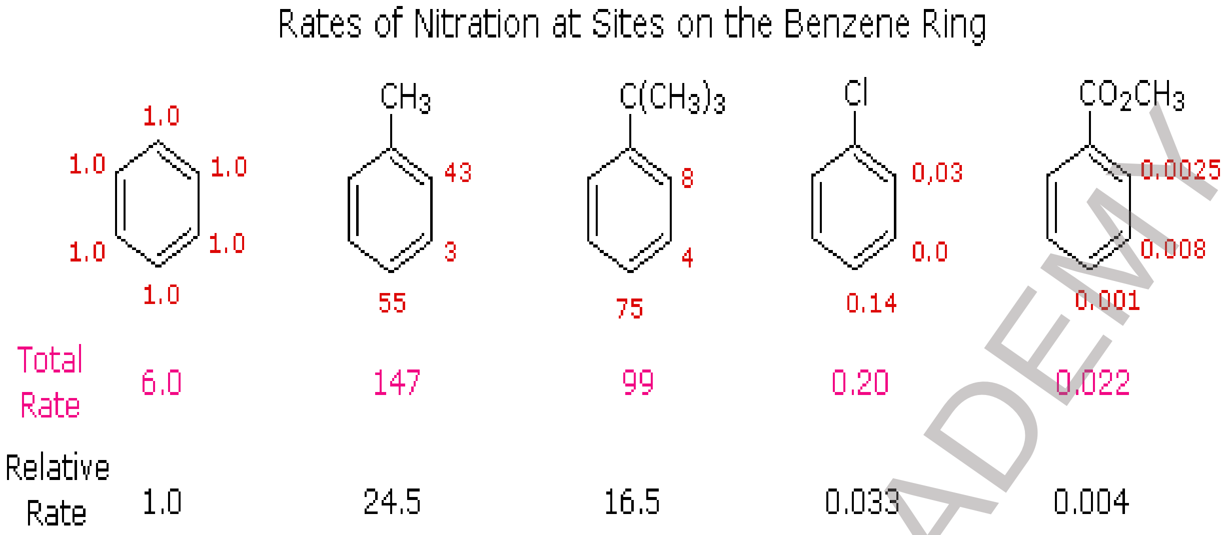
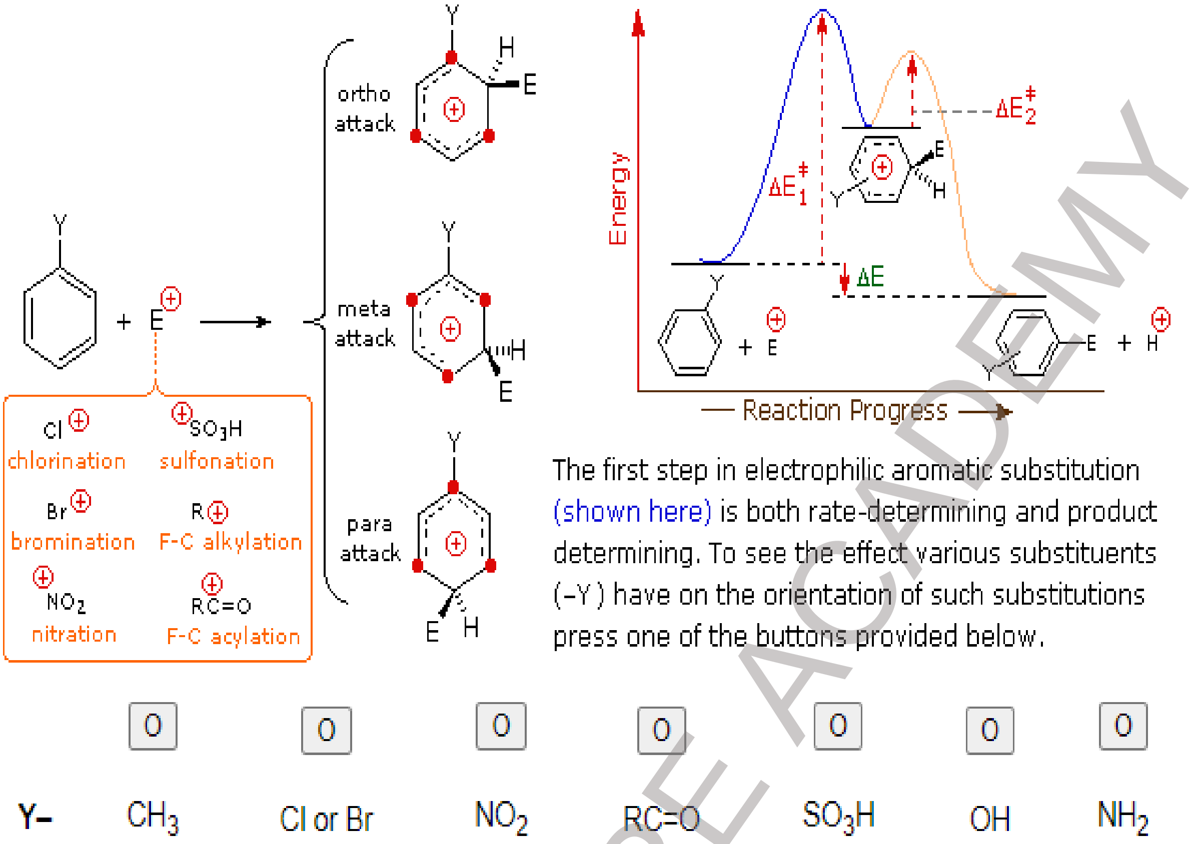


Figure 11: Indication of Rates of Nitration at sites on the Benzene ring

- From rate data of this kind, it is a simple matter to calculate the proportions of the three substitution isomers. Toluene gives 58.5% ortho-nitrotoluene, 37% para-nitrotoluene and only 4.5% of the meta isomer. The increased bulk of the tetra-butyl group hinders attack at the ortho-sites, the overall product mixture being 16% ortho, 8% meta and 75% para-nitro product. Although chlorobenzene is much less reactive than benzene, the rate of ortho and para-substitution greatly exceeds that of meta-substitution, giving a product mixture of 30% ortho and 70% para-nitrochlorobenzene. Finally, the benzoic ester gave predominantly the meta-nitro product (73%) accompanied by the ortho (22%) and para (5%) isomers, as shown by the relative rates. Equivalent rate and product studies for other substitution reactions lead to similar conclusions. For example, electrophilic chlorination of toluene occurs hundreds of times faster than chlorination of benzene, but the relative rates are such that the products are 60% ortho-chlorotoluene, 39% para and 1% meta-isomers, a ratio similar to that observed for nitration.

- The manner in which specific substituents influence the orientation of electrophilic substitution of a benzene ring is shown in the following interactive diagram. As noted on the opening illustration, the product-determining step in the substitution mechanism is the first step, which is also the slow or rate determining step. It is not surprising, therefore, that there is a rough correlation between the rate-enhancing effect of a substituent and its site directing influence. The exact influence of a given substituent is best seen by looking at its interactions with the delocalized positive charge on the benzenonium intermediates generated by bonding to the electrophile at each of the three substitution sites. This can be done for seven representative substituents by using the selection buttons underneath in the **Figure 12.**



The first step in electrophilic aromatic substitution (shown here) is both rate-determining and product determining. To see the effect various substituents (-Y) have on the orientation of such substitutions press one of the buttons provided below.

Figure 12: Mechanism of electrophilic substitution reaction in Benzene ring

- In the case of alkyl substituents, charge stabilization is greatest when the alkyl group is bonded to one of the positively charged carbons of the benzenonium intermediate. This happens only for ortho and para electrophilic attack, so such substituents favor formation of those products. Interestingly, primary alkyl substituents, especially methyl, provide greater stabilization of an adjacent charge than do more substituted groups (note the greater reactivity of toluene compared with tert-butylbenzene). Nitro (NO_2), sulfonic acid (SO_3H) and carbonyl $(C=O)$ substituents have a full or partial positive charge on the atom bonded to the aromatic ring. Structures in which like-charges are close to each other are destabilized by charge repulsion, so these substituents inhibit ortho and para substitution more than meta substitution. Consequently, meta-products predominate when electrophilic substitution is forced to occur.
- Halogen (X), OR and NR_2 substituents all exert a destabilizing inductive effect on an adjacent positive charge, due to the high electronegativity of the substituent atoms. By itself, this would favor meta-substitution; however, these substituent atoms all have non-bonding valence electron pairs which serve to stabilize an adjacent positive charge by pi-bonding, with resulting delocalization of charge. Consequently, all these substituents direct substitution to ortho and para sites. The balance between inductive electron withdrawal and p-π conjugation is such that the nitrogen and oxygen substituents have an overall stabilizing influence on the benzenonium intermediate and increase the rate of substitution markedly; whereas halogen substituents have an overall destabilizing influence.

10.1.3. Characteristics of Specific Substitution Reactions

- The conditions commonly used for the aromatic substitution reactions discussed here are repeated in the table on the right. The electrophilic reactivity of these different reagents varies. We find, for example, that nitration of nitrobenzene occurs smoothly at $95^{\circ}C$, giving meta-dinitrobenzene, whereas bromination of nitrobenzene (ferric catalyst) requires a temperature of $140^{\circ}C$. Also, as noted earlier, toluene undergoes nitration about 25 times faster than benzene, but chlorination of toluene is over 500 times faster than that of benzene. From this we may conclude that the nitration reagent is more reactive and less selective than the halogenation reagents.
- Both sulfonation and nitration yield water as a by-product. This does not significantly affect the nitration reaction (note the presence of sulfuric acid as a dehydrating agent), but sulfonation is reversible and is driven to completion by addition of sulfur trioxide, which converts the water to sulfuric acid. The reversibility of the sulfonation reaction is occasionally useful for removing this functional group. The Friedel-Crafts acylation reagent is normally composed of an acyl halide or anhydride mixed with a Lewis acid catalyst such as $AlCl_3$. This produces an acylium cation, R-$C \equiv O^{(+)}$, or a related species. Such electrophiles are not exceptionally reactive, so the acylation reaction is generally restricted to aromatic systems that are at least as reactive as chlorobenzene. Carbon disulfide is often used as a solvent, since it is unreactive and is easily removed from the product. If the substrate is a very reactive benzene derivative, such as anisole, carboxylic esters or acids may be the source of the acylating electrophile. Some examples of Friedel-Crafts acylation reactions are shown in the following **Figure 13.** The first demonstrates that unusual acylating agents may be used as reactants. The second makes use of an anhydride acylating reagent, and the third illustrates the ease with which anisole reacts, as noted earlier. The $H_4P_2O_7$ reagent used here is an anhydride of phosphoric acid called pyro phosphoric acid. Finally, the fourth example illustrates several important points. Since the nitro group is a powerful deactivating substituent, Friedel-Crafts acylation of nitrobenzene does not take place under any conditions. However, the presence of a second strongly-activating substituent group permits acylation; the site of reaction is that favored by both substituents.

Halogenation:

$$\begin{array}{lcll} C_6H_6 + Cl_2 \;\&\; heat & \longrightarrow & C_6H_5Cl & + HCl \\ \qquad FeCl_3 & & Chlorobenzene & \end{array}$$

Nitration:

$$\begin{array}{lcll} C_6H_6 + HNO_3 \;\&\; heat & \longrightarrow & C_6H_5NO_2 & + H_2O \\ \qquad H_2SO_4 catalyst & & Nitrobenzene & \end{array}$$

Sulfonation:

$$\begin{array}{lcll} C_6H_6 + R - Cl \;\&\; heat & \longrightarrow & C_6H_5SO_3H & + H_2O \\ \qquad AlCl_3 catalyst & & Benzenesulfonic\ acid & \end{array}$$

$$\begin{array}{llll} Alkylation: & C_6H_6 + R-Cl \,\&\, heat \longrightarrow & C_6H_5-R & + HCl \\ Friedel-Crafts & \quad AlCl_3\ catalyst & An\ Arene & \end{array}$$

$$\begin{array}{llll} Acylation: & C_6H_6 + RCOCl \,\&\, heat \longrightarrow & C_6H_5COR & + HCl \\ Friedel-Crafts & \quad AlCl_3\ catalyst & An\ Aryl\ Arene & \end{array}$$

Figure 13: Illustration of Various substitution reactionin Benzene

The schematic representation of these reactions is shown in **Figure 14.**

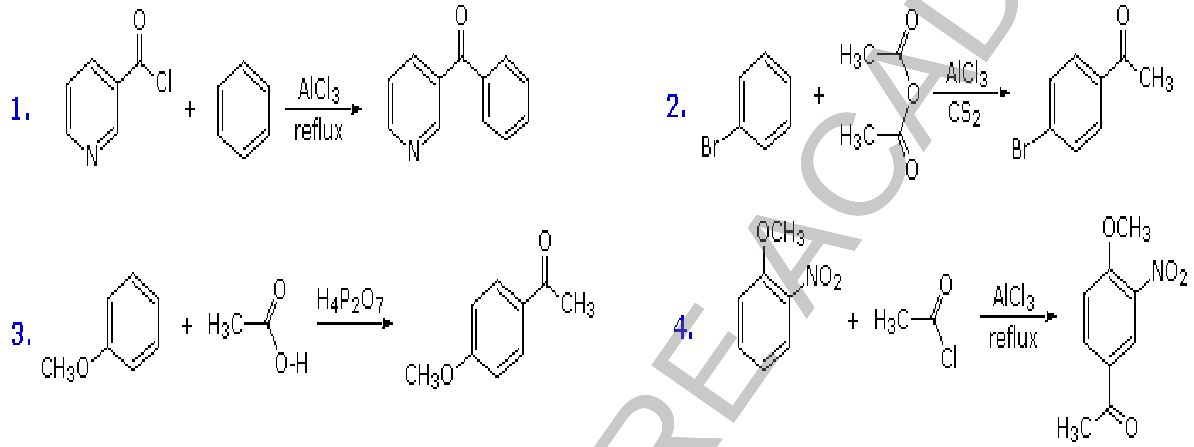


Figure 14: Schematic representation of electrophilic substitution reactions in benzene

- A common characteristic of the halogenation, nitration, sulfonation and acylation reactions is that they introduce a deactivating substituent on the benzene ring. As a result, we do not normally have to worry about di substitution products being formed. Friedel-Crafts alkylation, on the other hand, introduces an activating substituent (an alkyl group), so more than one substitution may take place. If benzene is to be alkylated, as in the following synthesis of tert-butylbenzene, the mono-alkylated product is favored by using a large excess of this reactant. When the molar ratio of benzene to alkyl halide falls below 1:1, para-ditert-butylbenzene becomes the major product.

$$C_6H_6(large\ excess) + (CH_3)_3C-Cl + AlCl_3 \longrightarrow C_6H_5-C(CH_3)_3 + HCl$$

- The carbocation electrophiles required for alkylation may be generated from alkyl halides (as above), alkenes + strong acid or alcohols + strong acid. Since $1^\circ -$carbocations are prone to rearrangement, it is usually not possible to introduce $1^\circ -$ alkyl substituents larger than ethyl by Friedel-Crafts alkylation. For example, reaction of excess benzene with 1-chloropropane and aluminum chloride gives a good yield of isopropyl benzene (cumene).

$$C_6H_6(large\ excess) + CH_3CH_2CH_2-Cl + AlCl_3 \longrightarrow C_6H_5-CH(CH_3)_2 + HCl$$

Additional examples of Friedel-Crafts alkylation reactions are shown in the following Figure 15.

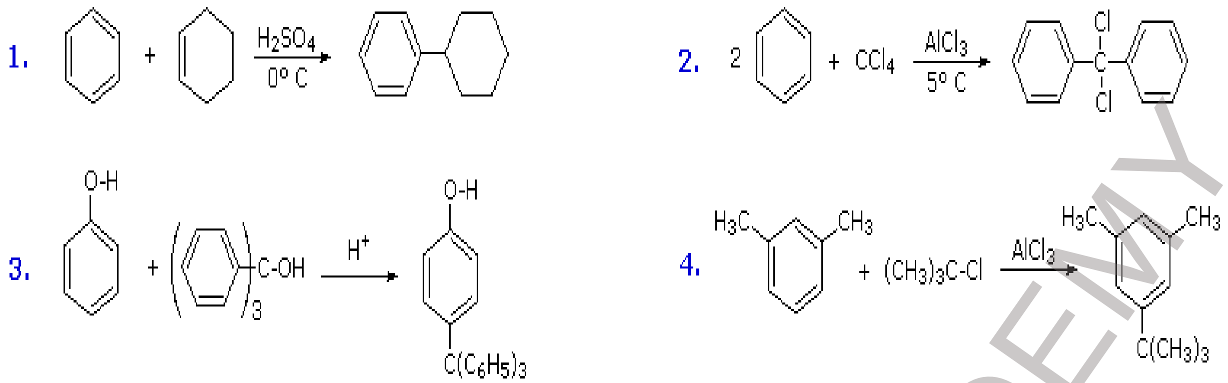


Figure 15: Examples for Friedel -Craft Alkylation Reactions

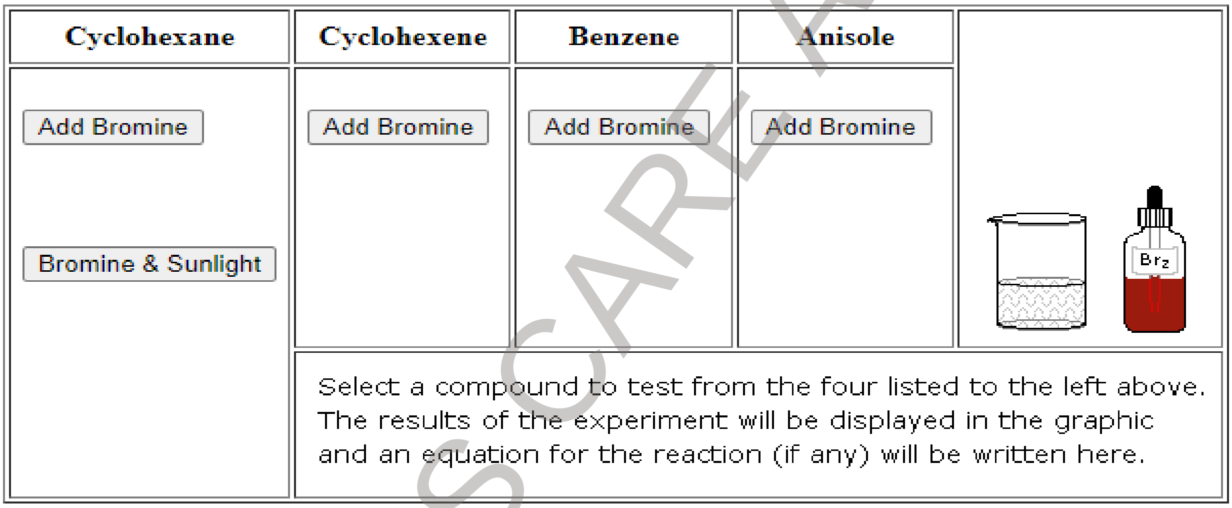
- The first and third examples show how alkenes and alcohols may be the source of the electrophilic carbocation reactant. The triphenylmethyl cation generated in the third case is relatively unreactive, due to extensive resonance charge delocalization, and only substitutes highly activated aromatic rings. The second example shows an interesting case in which a polychlororeactant is used as the alkylating agent. A fourfold excess of carbon tetrachloride is used to avoid tri-alkylation of this reagent, a process that is retarded by steric hindrance. The fourth example illustrates the poor orientational selectivity often found in alkylation reactions of activated benzene rings. The bulky tert-butyl group ends up attached to the reactive *meta*-xylene ring at the least hindered site. This may not be the site of initial bonding, since polyalkylbenzenes rearrange under Friedel-Crafts conditions (*para*-dipropyl benzene rearranges to *meta*-dipropyl benzene on heating with $AlCl_3$).

- A practical concern in the use of electrophilic aromatic substitution reactions in synthesis is the separation of isomer mixtures. This is particularly true for cases of ortho-para substitution, which often produce significant amounts of the minor isomer. As a rule, para-isomers predominate except for some reactions of toluene and related alkyl benzenes. Separation of these mixtures is aided by the fact that para-isomers have significantly higher melting points than their ortho counterparts; consequently, fractional crystallization is often an effective isolation technique. Since meta-substitution favors a single product, separation of trace isomers is normally not a problem.

10.1.4. Reactions of Bromine with Selected Compounds

- Bromine is a strong electrophile and has a characteristic red-brown color. These properties make bromine a useful reagent for probing the reactivity of colourlessnucleophilic organic compounds, such as alkenes and arenes. Two kinds of reaction are common: addition & substitution. In an addition reaction to an alkene two covalent C-Br bonds are formed, and the color of the bromine fades as the colorless product is generated. In a substitution reaction of a hydrocarbon a C-Br covalent bond is also formed, but this product is accompanied by release of of an equal molar quantity of hydrogen bromide gas. HBr is a colorless gas, having a nasty sharp, choking odor. The easiest way of detecting this gas is through its rapid reaction with ammonia (also a gas), which generates a cloud of ammonium bromide particles. The ammonia is conveniently introduced by way of an adjacent beaker containing ammonium hydroxide solution.

- The following unit provides a virtual demonstration of the reactions (or lack of reaction) of bromine with a selected group of compounds. Cyclohexane has no pi-unsaturation and is therefore not nucleophilic. It does not react with bromine unless energy in the form of light or heat is applied. In such a case a free-radical substitution reaction occurs. Cyclohexene is a typical alkene, and benzene and anisole are aromatic compounds. The methoxy substituent present in anisole increases the nucleophilicity of the aromatic ring, and greatly enhances the reactivity of the ring toward electrophilic attack. A small amount of the ortho substituted product is also obtained from the bromination of anisole is shown in the **Figure 16.**



Select a compound to test from the four listed to the left above. The results of the experiment will be displayed in the graphic and an equation for the reaction (if any) will be written here.

Figure 16: Isomer formation in Anisole

10.2. A General Mechanism for Electrophilic Aromatic Substitution: Arenium Ion Intermediates

- Benzene reacts with an electrophile using two fits electrons. This first step is like an addition to anordinarydoublebond.

Instep1:

- The electrophilere acts with two electrons from the aromatic ring.
- An electrophilic aromatic substitution consists of three main fundamental components: During the reaction, a new σ bond is formed from a $C=C$ in the arene nucleophile. Proton is removed by the breaking of $C-H$ σ bond. The $C=C$ is reformed which restores the aromaticity is shown in the **Figure 17.**

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