

Module5-1-Effective

Module-5: Periodic properties and Stereochemistry

[Effective nuclear charge, penetration of orbitals, variations of s, p, d and f orbital energies of atoms in the periodic table, electronic configurations, atomic and ionic sizes, ionization energies, electron affinity and electronegativity, polarizability, oxidation states, coordination numbers and geometries, hard soft acids and bases.]

Mendeleev:

Russian chemist. He proposed that the properties of the elements were a function of their atomic masses. He noticed that when the elements were arranged in order of increasing atomic mass certain similarities in their chemical properties appeared at regular intervals. Such a repeating pattern is referred to as periodic. His procedure left several empty spaces in his periodic table.....

“Physical and Chemical properties of elements are periodic functions of their atomic weights”

Moseley:

English chemist. He discovered that the elements in the periodic table fit into pattern when they were arranged in increasing order to the number of proton in the nucleus. He thought that the differences in the properties of the elements resulted from the amount of +chg in the nucleus. His work led to the modern definition of atomic number and the recognition that atomic number not the mass is the basis for the organization of the periodic table.

Periodic Law:

“The physical and chemical properties of elements are periodic functions of their atomic number”. That is, when the elements are arranged in order of increasing atomic number, elements with similar properties appear at regular intervals.

Modern Periodic Table:

Modern Periodic Table is an arrangement of elements in order of their atomic numbers so that elements with similar properties fall into the same column, or group.

Noble gases: First one, argon discovered in 1844, last one Radium in 1900, placed in group 18.

Lanthanides: 14 elements with atomic numbers from 58 (cerium, Ce) to 71 (Lutetium, Lu) because these elements are so similar they were difficult to tell apart.

Actinides: 14 elements with atomic numbers from 90 (thorium, Th) to 103 (Lawrencium, Lr). The lanthanides and actinides belong in periods 6 & 7 respectively between the elements of group 3 & 4. To save space they are usually set off below the main portion of the periodic table.

All the 112 known elements, either natural or synthetic, have been classified in the long form of a periodic table in accordance with their properties in such a way that elements with similar properties are grouped together in the same vertical column called group.

Most of the physical and chemical properties of the elements change periodically with the atomic number. Some of these properties such as effective nuclear charge, atomic size, ionization energy, and electron affinity are directly related to the electronic configuration of the atoms. On the other hand properties such as melting point and density are indirectly related to electronic configuration. The properties which are directly or indirectly related to their electronic configuration and show a regular graduation when we move from left to right in a period or from top to bottom in a group are called *periodic properties*.

ORGANIZING ELEMENTS :-

Periods & Blocks of the Periodic Table:-

Vertically arranged elements share similar chemical properties. The length of the Row's or periods determines the number of electrons that can occupy sub levels being filled in that period. The elements in the last column (Group 18) have filled sub levels.

Relationship Between Period length and Sub Levels Being Filled in the P.T.

Period Number	Number of Elements in Period	Sub Levels in Order of Filling
1	2	1s
2	8	2s 2p
3	8	3s 3p
4	18	4s 3d 4p
5	18	5s 4d 5p
6	32	6s 4f 5d 6p
7	-32-	7s 5f 6d, etc

Blocks:-Based on the Electron Configuration of the elements the periodic table can be sub divided into 4 sub levels blocks:-

s – block elements:-

Group 1 & 2: Chemically reactive metals. Group 1 outermost energy level contains a single 's' electron makes them very reactive known as alkali metals (Lithium, Sodium, Potassium, Rubidium, Cesium & Francium). So reactive they are never found free or uncombined in nature; usually stored in kerosene. All are silvery metals and soft enough to cut with a knife. Na & K are essential for living things. Group 2 Alkali earth metals. Two elements in the outermost energy level. Less reactive than alkali metals but are too reactive to be found in nature as free elements. Compound with Ca are among the most common materials in the earth's crust and are also important in biology. Be is very rare (aquamarines and emeralds are form of Be). Ra is a naturally occurring radioactive element that is very rare. Mg is used in strong, lightweight alloys for aircraft, truck bodies and ladders.

p – block elements:-

Group 13 – 18, prop vary greatly – on the right are non metals; on the left are metals; metalloids are along the zigzag line (B, Si, Ge, As, Sb, Se, Te, At). There are million of C compound that form the basis for organic chem. Oxygen is an important inorganic chem. that form compound with almost every elements and is present in most rocks and minerals. Group 17 elements are called halogens (salt former); they are most reactive non metal none found as free in nature; react vigorously with metals to form salts; all are diatomic molecules; reactivity decreases down the group. Al is the most important p – block metal because of the strong lightweight alloys it is used in.

d – block elements:- Group 3 - 12

They are metals with typical metallic properties; have high densities and high m.p., called the transition metals; play important roles in living organisms and are strong structurally useful materials. Less reactive elements. Such as Au, Pt, Ag, Cu are found free in nature and are so unreactive that they do not easily form compound with other elements. Tungsten has the highest m.p. of all the metals and is used as filaments in light bulbs. Ag compound are sensitive to light and are used in film. Colours is a common feature o the transition metal ions.

f – block:- The Lanthanides & Actinides, called inner transition metals. There are 14f – block elements in the 6 & 7 periods. Lanthanides are shiny metals with similar reactivity to Group 2 (alkali earth metals), 4f Sub level fills. Actinides are all radioactive and unstable; 5f sublevels fills.

CLSSIFICATION OF ELEMENTS ON THE BASIS OF ELECTRONIC CONFIGURATION:-

- **s – block elements:-**

$$ns^{1-2}; \text{ where } n = 1, 2, 3, \dots$$

The maximum value of n in configuration decides period and sum of valence electrons decides the group.

- **p – block elements:-**

$$ns^2 np^{1-6} \text{ where } n = 2, 3, 4, \dots$$

The maximum value of n in configuration decides period and sum of valence electrons decides the group.

- **d – block elements:-**

$$(n-1)d^{1-10} ns^{1-2} \text{ where } n = 4, 5, 6 \dots$$

The maximum value of n in configuration decides period and sum of valence electrons decides the group.

- **f – block elements:-**

$$(n-2)f^{0, 2, 3, \dots, 14} (n-1)^{0, 1, 2} ns^2 \text{ where } n = 6, 7 \dots$$

The maximum value of n in configuration decides period and sum of vience electrons decides the group.

PERIODIC PROPERTIES:-

There are many physical and chemical properties of elements, which show periodic variation with atomic number. Some of these properties such as valency, atomic size, ionization energy and electron affinity etc are directly related to the electronic configuration of the atom while some properties such as melting point, density etc are indirectly related to the electronic configuration.

Periodicity:

"The recurrence of similar properties of the elements after certain regular intervals when they are arranged in the order of increasing atomic numbers is called Periodicity."

The classification of the elements in certain facilities was based upon the observed similarities in the physical and chemical properties. But "why do certain elements exhibit similar properties recur at regular intervals of atomic numbers", were some important question yet to be answered.

SCREENING EFFECT:

In a multielectron atom, the electrons of the valence shell (outermost shell) are attracted towards the nucleus and also these electrons are repelled by the electrons present in the inner shells. On account of this, the actual force of attraction between the nucleus and the valence electron is somewhat decreased by the repulsive forces acting in opposite direction.

"The decrease in the force of attraction exerted by the nucleus on the valence electrons due to presence of electrons in the inner shells, is called SCREENING EFFECT OR SHIELDING EFFECT."

The magnitude of screening effect depends upon the no. Of inner electron i.e., greater the no. Of inner electrons, greater will be the value of the screening effect. The magnitude of the screening effect (σ) is determined by the **Slater's rules**.

$$\text{Screening constant} = \frac{\text{(ultimate shell electron-1)} \times 0.35 + \text{penultimate shell electrons} \times 0.85 + \text{Rest inner electrons} \times 1}{\text{Total number of inner electrons}}$$

The contribution of the inner electron to the magnitude of σ is calculated in the following ways:-

- A contribution of 0.35 unit from each electron of the orbit considered but the electron in consideration will have no contribution except for 1s electron for which a value of 0.30 seems to work better.
- A contribution of 0.85 units of screening effect from each electron of s, p-orbitals of penultimate orbit and 1.0 unit from d-orbital of the penultimate orbit.
- A contribution of 1.0 unit from each electron on any other inner orbits.

EFFECTIVE NUCLEAR CHARGE:

Due to screening effect the valence electron experiences less attraction towards nucleus. This brings decrease in the nuclear charge (Z) actually present on the nucleus; the reduced nuclear charge is termed **effective nuclear charge**.

Effective nuclear charge (Z^*) = Nuclear charge (Z) - Screening constant (σ)

Example:

Screening Constant and Effective Nuclear Charge of Argon atom:

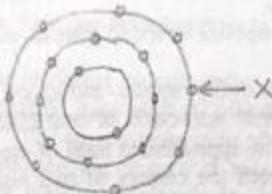


Fig:

Screening effect on electron marks X in Argon atom:

$$= 7 \times 0.35 + 8 \times 0.85 + 2 \times 1.0 \text{ Units}$$

$$= 11.25 \text{ Units}$$

$$\text{E.N.C. of Argon} = 18 - 11.25 = 6.75 \text{ Unit.}$$

Calculation of screening constant and E.N.C. of alkali metal for valence electron:

Down a group the value of Z^* increases slightly $Z - \sigma = \text{E.N.C.}$

Li (3)	2,1	$= 2 \times 0.85$	$= 1.7$	$3 - 1.7 = 1.3$
Na (11)	2,8,1	$= 8 \times 0.85 + 2 \times 1$	$= 8.88$	$11 - 8.88 = 2.2$
K (19)	2,8,8,1	$= 8 \times 0.85 + 10 \times 1$	$= 16.8$	$19 - 16.8 = 2.2$
Rb (37)	2,8,18,8,1	$= 8 \times 0.85 + 28 \times 1$	$= 34.8$	$37 - 34.8 = 2.2$

Calculation of screening constant and E.N.C. of member of second period for valence

		(σ)	$Z - \sigma = \text{E.N.C.}$
Li (2,1)	$= 2 \times 0.85$	$= 1.7$	$3 - 1.7 = 1.3$
Be (4)	$2,2$	$= 0.35 + 2 \times 0.85$	$= 2.05$
B (5)	$2,3$	$= 2 \times 0.35 + 2 \times 0.85$	$= 2.40$
C (6)	$2,4$	$= 3 \times 0.35 + 2 \times 0.85$	$= 2.75$
N (7)	$2,5$	$= 4 \times 0.35 + 2 \times 0.85$	$= 3.10$
O (8)	$2,6$		$= 4.55$

The E.N.C. increases in a $\frac{1}{5}$ fraction from L to O

F (9) 2,7

Ne (10)

$= 5.20$

$= 5.85$

Module5 (3)-IE

Ionization Energy/Ionization Potential:

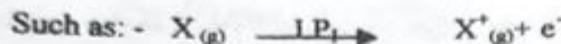
Ionization Potential:

The electrons are raised to higher energy levels by absorption of energy from an external source. If this process is continued, a stage comes when the electron goes completely out of the influence of the nucleus and a positive ion is produced.
"The amount of energy required to remove the most loosely bound electron (i.e., the outermost electron) from an isolated gaseous atom of an element in its lowest energy state (i.e., ground state) to produce a cation is known as Ionization Potential or Ionization Energy."

Such as:- $X_{(g)} \xrightarrow{I.P} X^+_{(g)} + e^-$
It is measured in unit of electron Volt(ev) per atom or K.J. per mole .

SUCCESSIVE IONIZATION POTENTIAL:

The electrons are removed in stages one by one from an atom. The amount of energy required to remove the first electron from a gaseous atom is called its first ionization potential. The energy required to remove the second electron from the atom is called second ionization potential. Similarly we have third, fourth ... ionization potential.



...

$$I.P_1 < I.P_2 < I.P_3$$

Increasing order of ionization potential is called *successive ionization potential*

First, second ,third, fourth and higher ionization energy:

Sodium form Na^+ ions magnesium form Mg^{+2} ions and aluminum form Al^{+3} ions. But have you ever wondered why Sodium does not form Na^{+2} ions or even Na^{+3} ions?

The answer can be obtained from data for the second , third and higher ionisation energy of the elements.

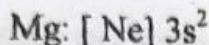
It does not take much energy to remove one electron from a sodium atom to form an Na^+ ion. Once this is done, however, it takes almost 10 times as much energy to break into this filled -shell configuration to remove a second electron. Because it takes more energy to remove the second electron than is given off in any chemical reaction, sodium can react with other elements to form compounds that react with other elements to form compounds that contain Na^+ ions not Na^{+2} or Na^{+3} ions.

First, second, third, fourth and higher ionization energies of Sodium, Magnesium and Aluminum (KJ/mol)

	1 st I.E	2 nd I.E	3 rd I.E	4 th I.E
Na	495	4562	6912	9543
Mg	737	1450	7732	10,540
Al	577	1816	2744	11,577

The first ionisation energy of sodium is the energy it takes to remove one electron from a neutral atom. The energy required to form a Na^{+3} ion in the gas phase is the sum of the first, second and third ionisation energies of the element.

When the ionisation energy of magnesium are analyzed. The first ionisation energy of magnesium is larger than sodium because magnesium has one proton in its nucleus to hold on to the electrons in the 3s orbital.



The second ionisation energy of Mg is larger than the first because it always takes more energy to remove an electron from a positively charged ion than from a neutral atom. The ionisation energy of magnesium is enormous, however, because of Mg^{+2} ion has a filled -shell electron configuration.

Measurement of Ionization potential:

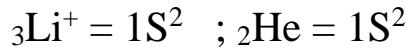
The experimental values of ionization energy are determined either by spectroscopic methods or by passing an electric current of gradually increasing intensity through the vapor of the element in a discharge tube.

Q. I.E of (Neon) Ne is more than Fluorine (F)?

Answer: The nuclear charge of Ne ($Z=10$) has been more than that of F ($Z=9$). Greater the nuclear charge, greater will be the force of attraction between nucleus and outermost electron. Hence the first I.P of neon would be greater than that of fluorine.

Q. I.E of Li^+ > I.E of He

Answer:



The I.E. of Li^+ has been more than that of helium. The reason for this is that the nuclear charge of Li ($Z=3$) is more than that of He ($Z=2$). High nuclear charge would be able to attract the same number of electrons ($Z=2$) with greater force. Hence high energy would be required to remove electron from Li^+ .

FACTORS AFFECTING THE VALUE OF IONISATION POTENTIAL:

- **Size of atom or ion:** The larger the atomic size, lesser is the value of ionization potential.
- **Screening effect:** Higher the screening effect, lesser is the value of ionization potential.
- **Nuclear Charge:** The higher the nuclear charge (proton in nucleus) the higher is ionization potential. Because of the higher nuclear charge, the electrons are bound with more force and hence higher shall be the energy required for its removal.

The value of ionization potential generally increases in moving from left to right in a period, since the nuclear charge of the elements (i.e., atomic number) also increases in the same direction.

Elements of 2 nd period : Li	Be	B	C	N	O	F	Ne
Nuclear Charge :	+3	+4	+5	+6	+7	+8	+9
IP(eV) :	5.4	<u>9.3</u>	<u>8.3</u>	11.3	<u>14.5</u>	<u>13.6</u>	17.4 21.6

The increase in the magnitude of I.P is due to the fact that the increase in nuclear charge the electrostatic attraction between the outermost electrons and the nucleus increases and hence it becomes comparatively more difficult to remove an electron.

- **Atomic radius:** With the increase in atomic radius, the ionization potential decreases. This is because of the fact that in case of larger atoms the attraction between the nucleus and outer-most electron is less and hence it is easier to remove an electron from a larger atom than from a smaller one.

Elements of IA group: Li	Na	K	Rb	Cs
Covalent radii(A^0) : 1.55	1.90	2.35	2.48	2.67
I.P.(eV) : 5.3	5.1	4.3	4.2	3.9

- **HALF-FILLED AND FULL-FILLED ORBITALS:**

According to Hund's rule, atoms having half filled or completely filled orbital are comparatively more stable. Hence, more energy is needed to remove an electron from such atoms leading to higher value of ionization potential.

- **SHAPE OF ORBITALS:** s-orbital is more close to nucleus than the p-orbitals of the same orbit thus it is easier to remove electron from a p-orbital in comparison to s-orbital, the ionization potential follows the following order:- s>p>d>f orbital of the same orbit.
- **PRINCIPAL QUANTUM NUMBER:-** Higher the value of n, lower will be ionization potential.
- **EFFECTIVE NUCLEAR CHARGE:** Higher the value of E.N.C, higher will be ionization potential.
- **ELECTRONEGATIVITY:** More the value of electronegative, higher will be ionization potential.

APPLICATION OF IONISATION POTENTIAL:

- To determine the no. of valence electrons in an atom:

The knowledge of ionization potential can also be used to find out the number of valence electrons in an atom. For example in case of Li the value of $I.P_1$ and $I.P_{II}$ are 5.4eV and 75.eV. These values show that one electron can much more readily be removed than the other. Thus there is only one electron in the valence shell of Li atom.

- **Relative reactivity of elements:**

Higher value of ionization potential of element is less reactive and vice-versa.

- **Reducing power of an element:**

Lower the value of ionization potential of an element, the greater is its reducing power.

- **Basic character of an element:**

Lower the value of ionization potential, greater will be the basic character of the element concerned.

PERIODIC TREND OF IONISATION POTENTIAL:

(A) Variation along a period:

In general , the ionisation energy increases with increasing atomic number in a period.

This is quite clear from the value of I.P of the second period elements are :

Elements of 2 nd period : Li	Be	B	C	N	O	F	Ne	
Nuclear Charge	: +3	+4	+5	+6	+7	+8	+10	
IP(eV)	: 5.4	<u>9.3</u>	<u>8.3</u>	11.3	<u>14.5</u>	<u>13.6</u>	17.4	21.6

The general increase along a period can be explained on the basis of atomic size and nuclear charge. We know that:-

1. on moving across a period from left to right , the nuclear charge increases.
2. The atomic size decreases along a period though the main energy level remains the same.

As a consequence of increased nuclear charge and simultaneous decrease in atomic size, the valence electrons are more and more tightly held by nucleus. Therefore, more or less energy is needed to remove the electron and hence, ionisation energy keeps on increasing.

(B) Variation along a group:

Within a group , there is gradual decrease in ionisation energy in moving from top to bottom.

The I.P value of the elements of first group

Elements of IA group: Li	Na	K	Rb	Cs	
I.P.(eV)	: 5.3	5.1	4.3	4.2	3

The decrease in I.E. down a group can be explained in terms of net effect of the following factor:

1. In going from top to bottom in a group the nuclear charge increases.
2. There is a gradual increase in atomic size due to an additional main energy shell(n).
3. There is increase in shielding effect on the outermost electron due to increase in the number of inner electrons.

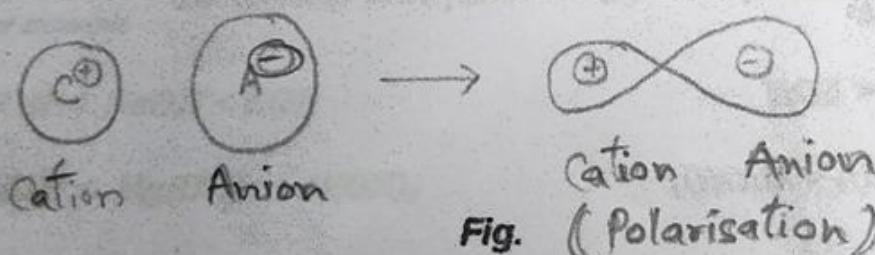
Polarizability:

POLARISING POWER AND POLARISABILITY: (Fajans Rule) (Polarizing power of the cation and Polarizability of the anion)

Ionic and Covalent bonds are two extreme types of bonds. In fact, most of the heteronuclear bonds have intermediate character. Even in case of pure ionic compound, there is some degree of covalent character. Fajans suggested that when a positive ion comes near a negative ion, polarization in ions will take place during their electrostatic attraction. This will distort the shape of positive as well as that of negative ion. The electron cloud of negative ion comes near the positive ion and this will more or less decrease the ionic character of the bond, increasing the covalent character.

"The ability of the cation to polarize the negative ion is known as its polarizing power, whereas the ability of an anion to polarize itself towards the cation is known as its polarizability."

"If there is no polarization, the bond will be ionic, if the degree of polarization is small, the bond will be ionic with some covalent character and if the polarization is more, the covalent character becomes predominant".

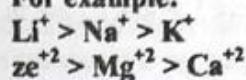


FACTOR EFFECTING THE POLARISING POWER OF CATION:

The polarizing power of cation or ionic potential will be maximum when it has:-

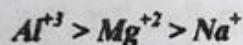
- Very Smaller Size: (The polarizing power of cation decreases moving downwards the group and it increases from left to right across the periods.)

For example:

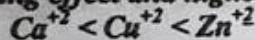


- Very Higher Charge:

For example:



- Greater number of d-electrons if they have same charge:
Greater is the number of d-electrons in the outer orbit of a cation, lower is screening effect and higher will be electron attracting effect.



FACTOR EFFECTING THE POLARISIBILITY OF ANION:

The polarizability of anions increases with:-

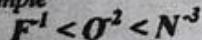
- Increases in its Size:

For example



- Increases in charge:

For example



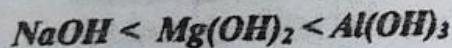
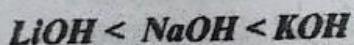
Following are the important application of the concept of polarization of ions:

Water solubility: Since ionic compounds are highly soluble in water and so increase in covalent character will decrease their degree of dissociation, decreasing water solubility.

Basic Character: -

It was found that the basic character of metal oxide or metal hydroxides decreases with the increase in the polarizing power of metal ion

For example



Thermal Stability:

Increase in the polarizing power of cation, will decrease the thermal stability of metal hydroxides.

Melting points of Compounds.

Magnetic Properties:

Paramagnetism:

The presence of one or more unpaired electrons is the cause of paramagnetism. A paramagnetism substance is attracted by an applied magnetic field.

Since most of the transition metal ions have unpaired d-electron, they show paramagnetic behavior.

Exception: Sc^{+4} , Ti^{+4} , Zn^{+2} , Cu^+ etc, which do not contain any unpaired electron and hence are diamagnetic.

Diamagnetism:

The absence of unpaired electrons is the cause of diamagnetism. A diamagnetism substance will be repelled by an applied magnetic field.

Ferromagnetism:

It is a special property observed in some substances in the solid state (not in solution). It is due to large number of unpaired electrons. The substance remains magnetized even after applied magnetic field is removed.

The most common example is of Fe followed by Co and Ni

In terms of n (number of unpaired electron) magnetic moment is given by the formula:

$$\mu = \sqrt{n(n+2)}$$

$$\text{Thus when, } n=1, \mu = \sqrt{1 \times 3} = 1.73 \text{ B.M}$$

$$n=2, \mu = \sqrt{2 \times 4} = 2.83 \text{ B.M etc}$$

$$1 \text{ B.M} = e h / 4\pi m c$$

Where e = electronic charge, h = Planck's constant, m = mass of the electron

c = speed of light

NON-STOICHIOMETRY:

A feature of the transition elements is that they sometimes form non-stoichiometric compounds. These are compounds of indefinite structure and properties.

For example:-

Iron (II) oxide FeO should be written with a bar over the formula FeO to indicate that the ratio of Fe and O atoms is not exactly 1:1, analysis shows that the formula varies between $\text{Fe}_{0.94}\text{O}$ and $\text{Fe}_{0.84}\text{O}$.

Non-Stoichiometry is shown particularly among transition metal compounds of the Group 16 elements (O, S, Se and Te). It is mostly due to the variable valency of transition elements.

Sometimes non-stoichiometry is caused by defect in the solid structures.
Colored Compounds:

Most of the compounds of d-block elements are colored in the solid state or in the solution. All those salts in which incomplete d-orbital are present, absorb part of the visible light and remaining portion is reflected. The salts having the metal ions possessing configurations either $(n-1)d^0$ or $(n-1)d^{10}$ are colorless because absorption of light doesn't take place.

The absorbed light is used for shifting of electron or electrons from one energy level to the other in d-orbital. The following examples justify this statement.

Sc^{+3} $3d^{10}$ Colorless	Ti^{+4} $3d^0$ Colorless	Cu^+ $3d^{10}$ Colorless	Zn^{+2} $3d^{10}$ Colorless	Cd^{+2} $3d^{10}$ Colorless	Ag^+ $3d^{10}$ Colorless
Fe^{+2} $3d^6$ Pale green	Fe^{+3} $3d^5$ Yellow	Cr^{+3} $3d^3$ Green	V^{+3} $3d^2$ Pink	Co^{+2} $3d^7$ Pink	Ni^{+2} $3d^8$ Green

Color of the salts:

There is a close relationship between the percentage of ionic character and the color of the salt.

1. If the ionic character of the bond is less than 20%, the compound is colored.
2. If it more than 20%, the compound is colorless.
3. If ionic character becomes lesser and lesser than 20%, the compound takes on color passing through yellow and orange to red and black, i.e., color goes on deepening.

Example:

AgCl	--- White
AgBr	--- Pale Yellow
AgI	--- Yellow
Ag ₂ S	--- Black

To determine the percentage ionic character:-

$$\% \text{ Ionic character} = 16(X_A - X_B) + 3.5(X_A - X_B)^2$$

In A B type compound

X_A = electronegativity of A

X_B = electronegativity of B

Geometry of Molecule:

9.11 GEOMETRY OF MOLECULE

It is a matter of common experience that every system tends to acquire a state of lowest energy or maximum stability. This also applies to the shape or geometry possessed by a molecule. The shape or geometry of a molecule may be defined as *the relative arrangement of the bonded atoms present in the molecule*.

As we have already studied, ionic bond is the result of electrostatic forces of attraction between the oppositely charged ions which are non-directional in nature. Due to this the shape of an ionic crystal is determined only by the relative sizes of the ions and the charges carried by them.

Covalent bonds, on the other hand, are directional and the shapes of covalent molecules are determined by the orientations of the bonds with respect to each other. We will be discussing here, the geometries of only some simple covalent compounds consisting of a few atoms.

9.11.1 Determination of Geometrical Molecules : VSEPR Theory

Valence Shell Electron Pair Repulsion theory or VSEPR theory constitutes a simple method for predicting the shapes of different molecules. According to this theory:

(i) *The shape of a molecule is related to the number of valence shell electron pairs around the central atom in a molecule.*

This is because there are strong repulsive forces operating between the valence shell electron pairs surrounding the central atom which tend to increase the energy of the system. For example, nitrogen in NH_3 has 4 electron pairs in its valence shell while boron in BF_3 has 3 electron pairs in its valence shell.

(ii) *Valence shell electron pairs around the central atom in a molecule tend to stay as far apart as possible.* This is because it would minimize the repulsive electronic interactions and thus lead to a state of minimum energy (and maximum stability) for the molecule.

(iii) *The orbital of a non-bonding or lone pair of valence shell electrons occupies more space than the orbital having bonding pair of electrons.*

This is because a non-bonding pair of electrons is under the influence of only one nucleus while the bonding pair is attracted by two nuclei. Due to the tendency of their orbitals to occupy more space, non-bonding pair of electrons repels the other pairs of electrons to a greater extent. Thus the repulsive interactions between non-bonding (or lone) pair of electrons and another lone pair of electrons is more than between lone pair and bond pair; which in turn is greater than that of the bond pair and bond pair repulsion. The repulsive interactions between different pairs of electrons may be summed up as:

lone pair — lone pair > lone pair — bond pair > bond pair — bond pair.

(iv) *When the central atom is surrounded only by similar bonded electron pairs, the repulsive interactions between electron pairs are similar and the molecular geometry is regular.*

(v) *When the central atom is surrounded by both bonded and lone pairs of valence electrons or by unequivalent bonded pairs, the repulsive interactions are not equivalent and the geometry is irregular.*

Some Important Generalization of VSEPR Theory

Based upon the postulates already listed, the following generalizations can be made regarding the shapes of simple molecules.

1. Molecules in which central atom is surrounded by two valence shell electron pairs.

A molecule having only two valence shell electron pairs around the central atom (such as A : B) would always have linear arrangement of atoms. This is because the linear arrangement puts the two pairs of valence shell electrons as far apart from each other as is possible and is thus the arrangement of lowest energy. That is why molecules such as BeF_2 and HgCl_2 have linear shape with the bond angles being 180° .

We might expect to find this geometry also in other molecules that have only two pairs of bonded electrons about a central atom. This is indeed so and molecules such as $\text{Cl}-\text{Be}-\text{Cl}$ and $\text{Cl}-\text{Zn}-\text{Cl}$ also have linear geometry.

2. Molecules in which central atom is surrounded by three valence shell electron pairs.

Let us now imagine a molecule such as AB_3 in which the central atom is surrounded by three pairs of valence shell electrons and the three atoms attached to the central atom are similar to one another. For the three electron pairs to have minimum repulsions between them, the pairs should be placed at the vertices of an equilateral triangle while the central atom is at the centre of the triangle. This gives rise to an equilateral triangular shape of the molecule with each bond angle being 120° . BF_3 affords a common example of such a molecule as depicted.

BCl_3 and MCl_3 have also got similar shapes.

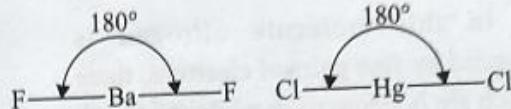


Fig. 9.11 Linear shapes of BeF_2 and HgCl_2 molecules.

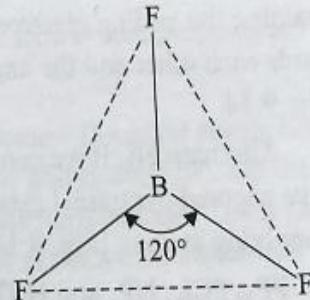


Fig. 9.12 Equilateral triangular shape of BF_3 molecule.

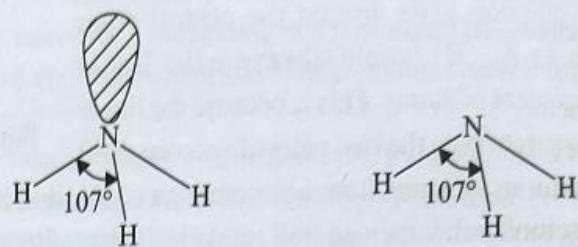
Shape of ammonia

In this molecule nitrogen is surrounded by four pairs of electrons, three of which are bonding pairs while the fourth is a non-bonding pair as shown below:

The four pairs of electrons should be directed towards the four vertices of a tetrahedron to have minimum repulsion. However, the orbital containing non-bonding electron occupies more space and also repels the orbitals containing bonding electrons to greater extent. As a result, the orbitals containing the ending electrons are pressed towards each other and the angle between them is compressed slightly from $109^{\circ}28'$ to 107° as shown in Fig. 9.14.

Alternatively, if we consider the orientations of only the three N-H bonds, ammonia may be said to have trigonal pyramidal geometry: the 3H atoms forming the triangular base of the pyramid with the N atom lying at apex [Fig. 9.14(b)].

PF_3 , PCl_3 , NP_3 and H_3O^+ also have similar shapes although bond angles are different.



(a) Nearly tetrahedral orientation of four valence shell electron pairs around nitrogen atom.

(b) Trigonal pyramidal shape showing the three N—H bonds.

Fig. 9.14

Shape of water

In case of water, the oxygen atom is again surrounded by four pairs of valence shell electrons but two of these pairs are bonding pairs while the other two are non-bonding pairs as shown below:



These four pairs of electrons should normally be directed towards the four vertices of a tetrahedron. However, due to the tendency of orbitals containing non-bonding electrons to occupy more space and to repel other orbitals to a greater extent, the orbitals of non-bonding electrons move away from each other. At the same time, the orbitals containing bonding electrons are forced to move closer to each other. This reduces the H—O—H bond angle from $109^{\circ}28'$ to $104^{\circ}28'$ as shown in Fig. 9.15. Distortion of bond angle is more here than in case of ammonia because of the presence of two non-bonding pairs of electrons as compared with only one non-bonding pair of electrons in ammonia. However if we consider only the orientations of two O—H bonds, then water may be described as bent or angular molecule with a bond angle of $104^{\circ}28'$.

H_2S , F_2O , SCl_2 and NH_2^- have similar shapes but different bond angles.

4. Molecules in which central atom is surrounded by five valence shell electron pairs.

PF_5 affords an example of a molecule in which central atom is surrounded by five pairs of valence shell electrons.

The geometry that minimizes the inter-electron pair repulsions and corresponds to a state of minimum energy is the trigonal bipyramidal structure as shown in Fig. 9.16. In this structure, three of the fluorine atoms lie in the same equatorial plane as the phosphorus atom and are, therefore, termed as equatorial fluorine atoms. The bonds linking these fluorine atoms to the central atom also lie in the same plane and are termed as **equatorial bonds**. The other two fluorine atoms lie above and below this equatorial plane on the axis of the bipyramid and are known as axial fluorine atoms. The bonds linking these two fluorine atoms to the central atom are termed as **axial bonds**.

It may be noted that PF_5 does not have a completely regular structure. The bond angles between the three equivalent equatorial bonds (marked *e*), which lie in the same plane, are 120° . On the other hand, the two axial bonds (marked *a*) which are similar to one another are at right angles to the plane of equatorial bonds, one being in a plane above and the other below the plane of the equatorial bonds (Fig. 9.16).

Another feature of the structure is that the axial P—F bonds are a bit longer (219 pm) than the equatorial bonds (204 pm). This is because the bond pair in axial P—F bond is being repelled by three bond pairs at 90° while the bond pair in equatorial P—F bond is being repelled by only two bond pairs

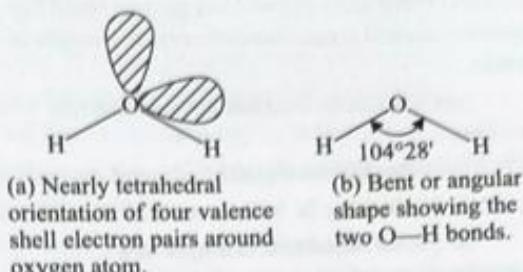


Fig. 9.15

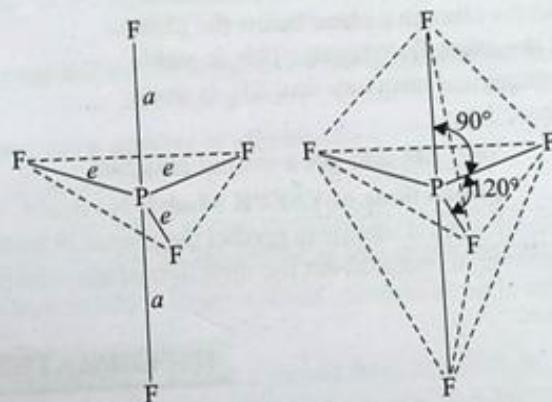


Fig. 9.16 Trigonal bipyramidal geometry of PF_5

at 90° ; the repulsive interactions between electron pairs at 120° at one another being negligible. As such the axial bond pairs experience greater repulsion from other bond pairs and, therefore, get farther away from the central atom. Accordingly, the length of the axial bonds is slightly more than that of equatorial bonds.

As a result of unsymmetrical structure which is less stable than a symmetrical one, PF_5 is highly reactive.

Similar structure is also adopted by PCl_5 , SbCl_5 , etc.

5. Molecules in which central atom is surrounded by six valence shell electron pairs.

SF_6 is an important example of a molecule in which the central atom is surrounded by six pairs of valence shell electrons.

To have minimum inter electron pair repulsions, the six pairs of electrons orient themselves octahedrally around the central S atom so that SF_6 has an octahedral structure as depicted in Fig. 9.17.

Four of the six S—F bonds lie in the same plane at right angles to one another. The other two are also at right angles to these, but one in a plane above and the other in a plane below the plane of the other four bonds. This is stable symmetrical structure and SF_6 is quite unreactive.

TeF_6 has also got a similar structure.

Limitations of VSEPR Model: No doubt, VSEPR model is able to explain the shape of simple molecules but is unable to predict the shapes in number of cases. Thus, it had a limited application only. Moreover, to think about the direction of electron pairs does not seem to be rational.

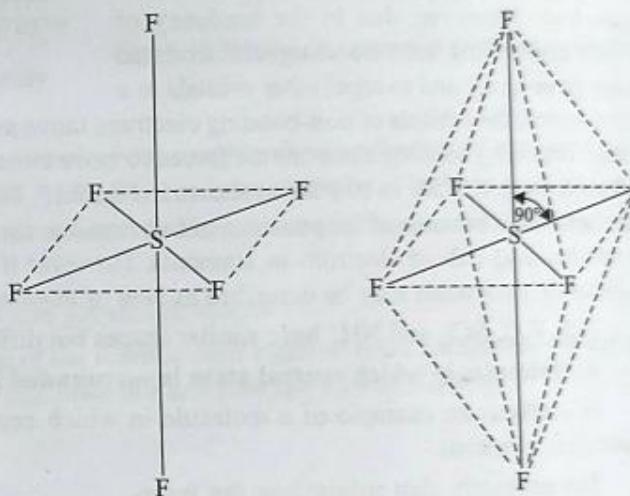


Fig. 9.17 Octahedral geometry of SF_6

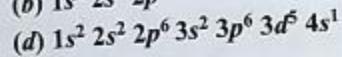
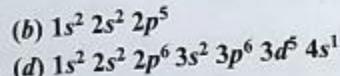
Module5-8-Question

Periodic Table Question:

PROBLEM WITH SOLUTIONS

Problem 1. From the electronic configurations of some elements given below, find:

- (i) Which elements belong to the same period?
- (ii) Which is a halogen?
- (iii) Which is a *d*-block element?
- (iv) Which element belongs to group 13?
 - (a) $1s^2 2s^2 2p^6 3s^2$
 - (c) $1s^2 2s^2 2p^6 3s^2 3p^1$
 - (e) $1s^2 2s^2 2p^6 3s^2 3p^6$



Solution.

- (i) (a), (c) and (e) belong to the same period
- (ii) (b) is a halogen
- (iii) (d) is a *d*-block element
- (iv) (c) belongs to group 13

Problem 2. The outer-electronic configurations of some elements are:

- | | |
|----------------------|------------------------|
| (i) $2s^2 2p^5$ | (ii) $3d^6 4s^2$ |
| (iii) $3d^{10} 4s^2$ | (iv) $3s^2 3p^6 4.5^1$ |

Solution.

- | | |
|---------------------------------|---------------------------------|
| (i) belongs to <i>p</i> -block | (ii) and |
| (iii) belong to <i>d</i> -block | (iv) belongs to <i>s</i> -block |

Problem 3. The electronic configuration of an element is $ns^2 np^5$. What is the group number of the element?

Solution. The group number of the element is 17. The electronic configurations convey that the element belongs to halogen which is just inner group to the last group of inert gases ($ns^2 np^6$).

Problem 4. How many elements are present in the 4th period of the periodic table?

Solution. 18 elements are present in the 4th period of the periodic table.

Problem 5. How many elements are in *d*-block?

Solution. 33 elements are in *d*-block.

Problem 6. What is the position of isotopes of an element in the periodic table?

Solution. They are placed in one position in the periodic table.

Problem 7. What is the position of isobars in the periodic table?

Solution. Isobars are atoms of the different elements having different atomic numbers but same mass number. They are placed at different places depending upon their atomic numbers without regard to atomic masses.

Problem 8. Arrange the following in order of increasing size:

- | | |
|--------------------------|---|
| (i) Na, K, Li | (ii) Cr, Ca ²⁺ , K ⁺ , S ²⁻ , Ar |
| (iii) I ⁺ , I | (iv) Li, Na, Be |

Solution.

- | | |
|--------------------------|---|
| (i) Li < Na < K; | (ii) Ca ²⁺ < K ⁺ < Ar < Cl ⁻ < S ²⁻ ; |
| (iii) I ⁺ < I | (iv) Be < Li < Na |

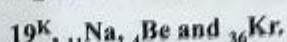
Problem 9. Which is larger in size in each of the following pairs:

- | | |
|--|---------------------------------------|
| (i) O, O ²⁻ | (ii) Al, Al ³⁺ |
| (iii) Li, F | (iv) Na ⁺ , F ⁻ |
| (v) Cu ⁺ , Cu ²⁺ | |

Solution.

- | | |
|---------------------|---------------------|
| (i) O ²⁻ | (ii) Al |
| (iii) Li | (iv) F ⁻ |
| (v) Cu ⁺ | |

Problem 10. Which out of the following has the largest ionisation energy?



Solution. ${}_{36}\text{Kr}$, being an inert gas, it has the most stable configuration and, therefore largest energy.

Problem 11. For each of the following pairs which one do you expect to have greater ionisation energy?

- | | |
|--------------|--------------------------|
| (i) Br, K | (ii) Li, Li ⁺ |
| (iii) Sr, Ra | (iv) Br, I |
| (v) O, S. | |

Solution.

- | | |
|----------|----------------------|
| (i) Br | (ii) Li ⁺ |
| (iii) Sr | (iv) O |

Problem 12. Which of the following has the largest ionisation energy: H, He, Ne, Be?

Solution. He, being an inert gas, it has stable electronic configuration ($1s^2$).

Problem 13. For each of the following pairs which one do you expect to have lower first ionisation energy?

- | | |
|---------------|---------------|
| (i) Cl or F | (ii) Ar or K |
| (iii) Cl or S | (iv) Kr or Xe |

Solution.

- | | |
|---------|---------|
| (i) Cl | (ii) K |
| (iii) S | (iv) Xe |

Problem 14. Which of the following elements will have (a) greatest electron affinity (b) smallest electron affinity?

(i) [Ne] $3s^2 3p^3$

(ii) [Ne] $3s^2 3p^4$

(iii) [Ne] $3s^2 3p^5$

(iv) [Ne] $3s^1$

Solution.

(i) Greatest electron affinity: [Ne] $3s^2 3p^5$

(ii) Smallest electron affinity: [Ne] $3s^2 3p^3$

Problem 15. Why are lanthanides and actinides placed in separate rows at the bottom of the periodic table?

Solution. This arrangement has been made due to the following reasons:

(i) to keep the elements having similar properties in a single row.

(ii) to avoid sidewise expansion of the periodic table.

Problem 16. What is the difference between ionization energy and electron affinity?

Solution. Ionization energy is the amount of energy required to remove the most loosely bound electron from an isolated atom in the gaseous state while electron affinity is the amount of energy released when an electron is added to an isolated atom in the gaseous state.

Problem 17. The first ionization energy of carbon is greater than that of boron whereas the reverse is true for the second ionization energy.

Solution. The first ionization energy of carbon is greater than boron as nuclear charge on carbon ($Z = 6$) is greater than the nuclear charge on boron ($Z = 5$).

The second ionization energy of boron is greater than carbon as the second electron has to be removed from $2s$ orbital of B^+ in $(1s^2 2s^2)$ which requires more energy than the removal of electron from $2p$ orbital of C^+ ion $(1s^2 2s^2 2p^1)$.

Problem 18. What is the difference between electron affinity and electronegativity?

Solution. Electron affinity is the amount of energy released when an electron is added to an isolated atom in the gaseous state. It is a measure of the attraction of the electron by an isolated atom.

Electronegativity is the relative tendency for an atom to attract the shared electron pair towards itself in a molecule. It is a measure for the attraction of electron pair in a molecule.

Problem 19. First ionisation energies of $5d$ elements are higher than $3d$ and $4d$ elements. Give reason.

Solution. This is due to the fact that outer valence electrons of $5d$ elements experience greater effective nuclear charge than $3d$ and $4d$ elements due to poor shielding of the nucleus by $4f$ electrons.

Problem 20. Why does Mn (II) is $3d^5$?

Solution. The electronic configuration of Mn is $3d^5 4s^2$ and that of Mn (II) is $3d^5$. All the $5d$ electrons are unpaired. It is this maximum possible number of unpaired electrons the d -orbitals which makes it most paramagnetic amongst bivalent ions of the first transition series.

Problem 21. Would you classify Zn as a transition element? Give reasons for your answers.

Solution. Zinc ($Z = 30$) has E. C[Ar] $3d^{10} 4s^2$. It has fully filled d -subshell in its elemental form as well as its common oxidation state i.e., Zn^{2+} in having $3d^{10}$ configuration. According to definition of transition

elements, it cannot be included in the transition elements. It does not show the characteristic properties of transition element, excepting its tendency to form complexes. But it is classified with transition elements because the last electron enters in the d -orbitals of its penultimate shell.

Problem 22. First ionisation energy of copper is higher than those of alkali metals while second and third energies are lower. Explain.

Solution. Cu has $[Ar]3d^{10} 4s^1$ configuration. As filled $3d$ sub shell is much less effective in shielding the outer s -electron than a noble gas shell present in alkali metals, so the $4s$ electron of copper is more tightly bound than in alkali metals. Hence, its first ionisation energy is higher than similar values for alkali metals. However, 2nd and 3rd ionisation energy values of copper are lower as compared to those of alkali metals due to the loss of electron from diffused d -orbital, while 2nd ionization energy in alkali metal would be very high as this electron is being removed from a noble gas core.

Problem 23. Iron is a transition element but sodium is not? Explain.

Solution. Iron has electronic configuration $[Ar] 3d^6 4s^2$ while sodium has electronic configuration $[Ne]3s^1$. Thus in iron last electron enters a d -orbital, so it is a transition element while in sodium last electron enters s -block element.

Problem 24. "The complexes of first transition series are mainly high-spin while those of second and third transition series are of low – spin type". Explain.

Solution. The elements of the first transition series, i.e., from Sc to Zn involve filling of $3d$ -orbitals. As compared to $4d$ and $5d$ orbitals, the $3d$ orbitals are relatively small in volume. Therefore, Inter electronic repulsion, which may come into play due to occupation by two electrons in an orbital (low spin) would be very large. Therefore, crystal field splitting for $3d$ block of elements is small. First row transition metals prefer to form high spin complexes.

On the other hand, in the second and third transition series, $4d$ and $5d$ orbitals have bigger sizes than $3d$ orbitals. Therefore, in the second and third transition series, Inter electronic repulsion are quite small. Hence, crystal field splitting energy is quite high which result in low spin complexes.

Problem 25. What justification is there for classifying Zn, Cd and Hg as transition elements? Give reasons.

Solution. The electronic configuration of Zn, Cd, and Hg can be expressed as $(n - 1)d^{10} ns^2$. Therefore, in their elemental form they cannot be classified as transition metals. These elements exhibit +2 oxidation state in their compounds. The M^+ ions, have $(n - 1)d^{10}$ configuration. Therefore, these elements neither in their elemental form, nor in their predominant oxidation state can be classified as transition elements, as they don't possess partially filled d -orbital. These elements, however, like transition metals, form a variety of complexes particularly with ammonia, amines, halides and cyanide ions and thus exhibit some resemblance.

Problem 26. Explain, why the second ionization energies for copper and chromium are anomalously high?

Solution. Cu = $[Ar]3d^{10} 4s^1$ and Cr = $[Ar]3d^5 4s^1$.

Their first ionization energies are low because removal of one electron gives a stable $3d^{10}$ or $3d^5$ configuration. Their second ionization energies are expected to be high because of removal of an electron from stable completely filled orbital $3d^{10}$ for Cu^+ and half filled orbital $3d^5$ for Cr^+ .

Problem 27. Why do the transition elements form complexes readily?

Solution. The transition elements form complexes due to

- (a) their small cation size
- (b) high effective nuclear charge
- (c) availability of vacant $(n-1)d$ orbitals of appropriate energy for accepting lone pairs of electrons donated by ligand.

Problem 28. Calculate the oxidation state of the metal ion in the following complexes:

- | | |
|-----------------------------|-------------------|
| (i) $K_3[Fe(CN)_6]$ | (ii) $[Ni(CO)_4]$ |
| (iii) $[Cu(C_2O_4)_2]^{2-}$ | |

Solution.

- | | |
|----------|--------|
| (i) +3 | (ii) 0 |
| (iii) +2 | |

Problem 29. How many ions per mole of the following complexes are present in the solution?

- | | |
|--------------------------|-----------------------|
| (i) $[Cr(NH_3)_5]Cl_2$ | (ii) $[Ag(NH_3)_2Cl]$ |
| (iii) $[Co(NH_3)_6]Cl_3$ | |

Solution.

- | | |
|---------|--------|
| (i) 3 | (ii) 2 |
| (iii) 4 | |

Problem 30. How many moles of Cl^- ion are furnished by one mole of each of the following?

- | | |
|----------------------------|-------------------------|
| (i) $[Pt(NH_3)_4Cl_2]Cl_2$ | (ii) $Na_2[PtCl_6]$ |
| (iii) $[Pt(NH_3)_4Cl_3]Cl$ | (iv) $[Cr(NH_3)_3]Cl_3$ |

Solution.

- | | |
|---------------|------------|
| (i) 2 mol | (ii) zero |
| (iii) one mol | (iv) 3 mol |

Problem 31. Explain that ionisation energy of neon is more than any other element of the second period.

Solution. Noble gases have the highest ionization energy in their respective periods. For example, ionization energy of Ne is more than any other element of the second period. So is the case with Ar. This is due to the fact that $ns^2 np^6$ arrangement which occurs in noble gases is highly stable and hence larger amount of energy is needed to remove an electron from this stable arrangement.

Problem 32. Which of the following elements has the highest electron affinity? Give reasons.

- | | |
|------------------------|-----------------------|
| (i) $[Ne] 3s^2 3p^3$ | (ii) $[Ne] 3s^2 3p^4$ |
| (iii) $[Ne] 3s^2 3p^5$ | |

Solution. The element (chlorine) corresponding to the electronic configuration (iii) will have the highest electron affinity. This is due to the reason that it contains one electron less than the stable noble gas configuration, i.e., $[Ne] 3s^2 3p^6$ and hence, has a strong tendency to accept one electron to acquire the stable noble gas configuration.

Questions:

R and S Notation

10.9 CONFIGURATION ON THE BASIS OF R AND S NOTATIONS

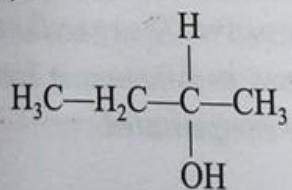
Cahn, Ingold and Prelog suggested a very simple procedure to specify a particular configuration in terms of prefixes R or S. The letter R is taken from Rectus and S from Sinister. The procedure involves the following two steps:

Step 1. The four atoms or groups of atoms bonded to the chiral centre are assigned a sequence of priorities in accordance with a set of rules known as sequence rules.

Sequence Rules

The sequence rules are as follows:

- (i) If all the four atoms directly attached to the chiral centre are different from one another, sequence of priorities is determined by atomic number. The atom of highest atomic number gets the highest priority while the one with the lowest atomic number comes last in order of priority. For example, in the compound 1-bromo-1-chloro-ethane, $\text{CH}_3\text{CH}(\text{Cl})\text{Br}$, the sequence of priorities will be Br, Cl, C, H.
- (ii) If two or more atoms directly attached to the chiral centre have the same atomic number, the relative priorities may be fixed by comparing the next atoms in the groups. If even this does not solve the problem, the comparison may be extended to the next atom and so on. For example, in sec-butyl alcohol,



the relative priorities of CH_3 and C_2H_5 are decided as follows. Each of these groups is linked to the chiral centre through the same atom, i.e., carbon. The next atoms in CH_3 are H, H and H while in C_2H_5 they are C, H and H. Since carbon has a higher atomic number than hydrogen, C_2H_5 gets higher priority.

(iii) If a group has an atom X linked to some other atom by double or triple bond, X is considered

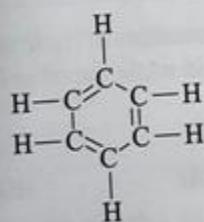
$\begin{array}{c} \text{H} \\ | \\ \text{C}=\text{O} \end{array}$
equivalent to two or three such atoms. For instance, if we compare the H groups, $\begin{array}{c} \text{H} \\ | \\ \text{C}=\text{O} \end{array}$ and $-\text{CH}_2\text{OH}$, the former gets higher priority as the next atoms in it are equivalent to O, O, H while in CH_2OH they are O, H, H.

It may be noted, however, that if in a group two or three atoms of X are separately linked to some atom through single bonds, such a group would get priority over the group containing doubly or triply bonded X. For example, let us compare the groups $\begin{array}{c} \text{H} \\ | \\ \text{C}=\text{CH}_2 \end{array}$ and $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}-\text{CH}_3 \end{array}$. In both these groups,

$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}-\text{CH}_3 \end{array}$ the next atoms will be taken as C, C, H. However, in $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}-\text{CH}_3 \end{array}$, the two carbons are actually attached through single bonds while in $\begin{array}{c} \text{H} \\ | \\ \text{C}=\text{CH}_2 \end{array}$ there is only one carbon attached through double bond. As such the group $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}-\text{CH}_3 \end{array}$ gets priority over $\begin{array}{c} \text{H} \\ | \\ \text{C}=\text{CH}_2 \end{array}$.

Similarly C_6H_5- (i.e., ) gets priority over $-\text{CH}=\text{CH}-$ which in turn gets priority over $-\text{CH}=\text{CH}_2$.

Note. The phenyl group  is considered as if it has one of Kekule structures that is:



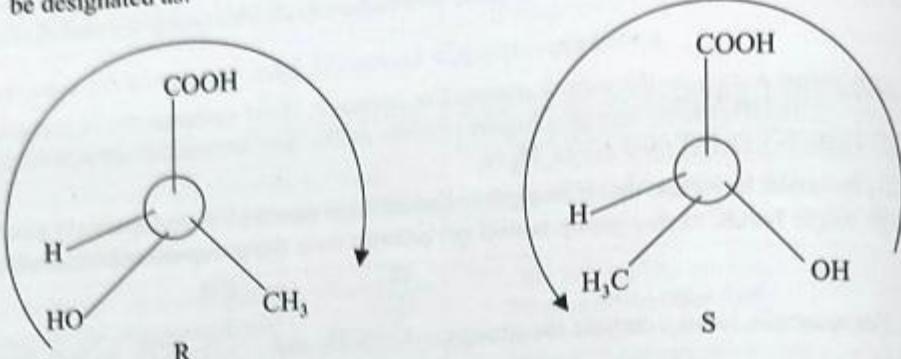
As such the atoms next to the carbon attached to chiral centre are treated as C, C and C.

Step 2. After deciding the sequence of priorities, the molecule is imagined to be in a position where the group of lowest priority is directed away from us. Now, we look at the arrangement of remaining groups in decreasing order of their priorities. If in doing so, the eye travels in clockwise direction, the configuration is specified as R. (Latin: rectus = right). If, on the other hand, the eye travels in anticlockwise direction, the configuration is specified as S (Latin: sinister = left).

Above rules are further explained by considering some specific examples:

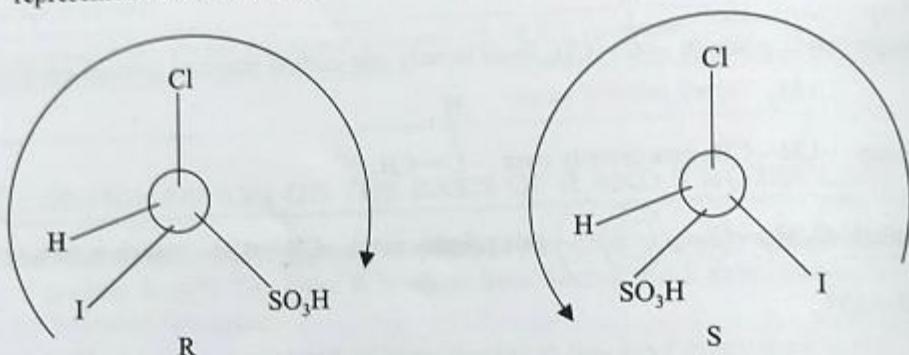
(i) Lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$.

The sequence of priorities is OH, COOH, CH_3 , H. Therefore, the specific configuration may be designated as:



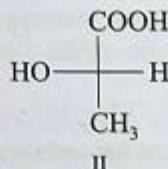
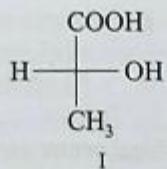
(ii) Chloriodomethane sulphonic acid, $\text{CH}(\text{Cl})(\text{I})\text{S}_3\text{OH}$.

The sequence of priorities is I, Cl, SO_3H and H. Therefore, R and S configurations may be represented as shown below:



10.10 SPECIFICATION OF CONFIGURATION

The configurations of the two enantiomers of lactic acid are I and II shown below. One of these configurations represents dextro or (+) acid while the other represents laevo or (-) lactic acid.



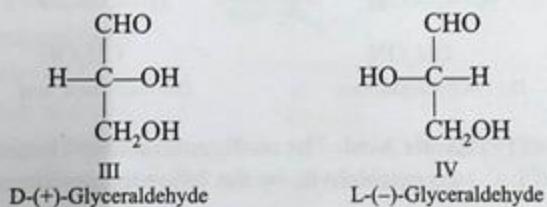
Specification of configuration means which one of the two enantiomers, (+) or (-), has the configuration I and which has the configuration II. In other words we do not know the **actual or absolute configuration** of each of the two enantiomers.

In the earlier days, it was not possible to determine the absolute configurations of the compounds. Fortunately, it is not always necessary to know the absolute configuration of an optically active compound. On the other hand, we are more interested in knowing the relative configurations of different compounds. For example, when an optically active compound undergoes a chemical reaction, we are mainly interested in whether the configurations of the reactant and its product are same or different and not in their actual configurations.

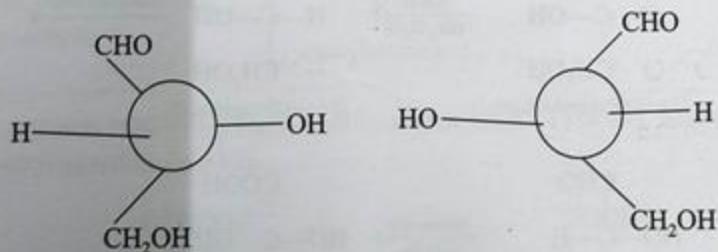
(A) Relative configurations by D and L Notation

It was proposed by Emil Fischer (1885) that a *standard reference compound* should be chosen to assign relative configurations to various optically active compounds. The compound chosen as the standard was **glyceraldehyde** ($\text{CH}_2\text{OHCHOHCHO}$) and its two enantiomers were designated by the symbols D and L. It must be made clear that the symbol D and L refer to configuration and are quite different from the prefixes *d* and *l* (read as "dextro" and "laevo") which refer to the direction of rotation. (+)-Glyceraldehyde was arbitrarily assigned the configuration III (in which the $-\text{OH}$ group attached to chiral carbon is towards right) and was given the symbol D. The (-) enantiomer was assigned the configuration IV (in which the $-\text{OH}$ group attached to chiral carbon is towards left) and was given the symbol L.

Planar Representation



Three Dimensional Representation



Reasons for selecting glyceraldehyde as the standard

Glyceraldehyde was chosen as the standard mainly because of the following reasons:

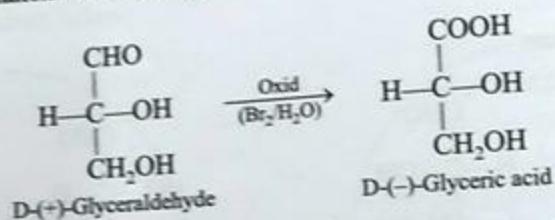
- (i) It is the simplest carbohydrate—an aldohexose its configuration could be easily related to those of the other important carbohydrates.

(ii) Since glyceraldehyde contains very reactive functional groups it could be converted into many other types of compounds. In this way it could be configurationally related to a large number of compounds.

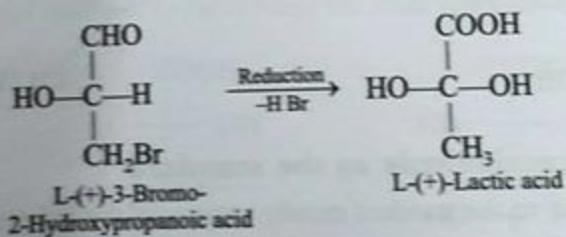
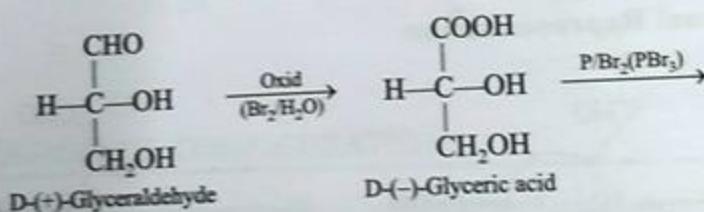
Correlation of Configuration

Many other compounds were then assigned relative configurations by relating their configuration to that of D- or L-glyceraldehyde. For this purpose either the compound under examination is converted into D- or L-glyceraldehyde or it is converted into the given compound by means of reactions which do not involve breaking of bonds to a chiral centre. The general principle involved in correlating the configurations of two compounds is that if a reaction does not involve the breaking of a bond about a chiral centre, the configuration about that chiral centre remains unchanged. Some important examples of the correlations of the configurations are given below:

(i) Configuration of (-)-Glyceric Acid: Glyceric (-)-acid can be obtained by the oxidation of D-(+)-glyceraldehyde as shown below. Since this reaction does not involve breaking of bonds about the chiral centre, (-)-glyceric acid must have the same configuration as that of glyceraldehyde taken i.e. D configuration.

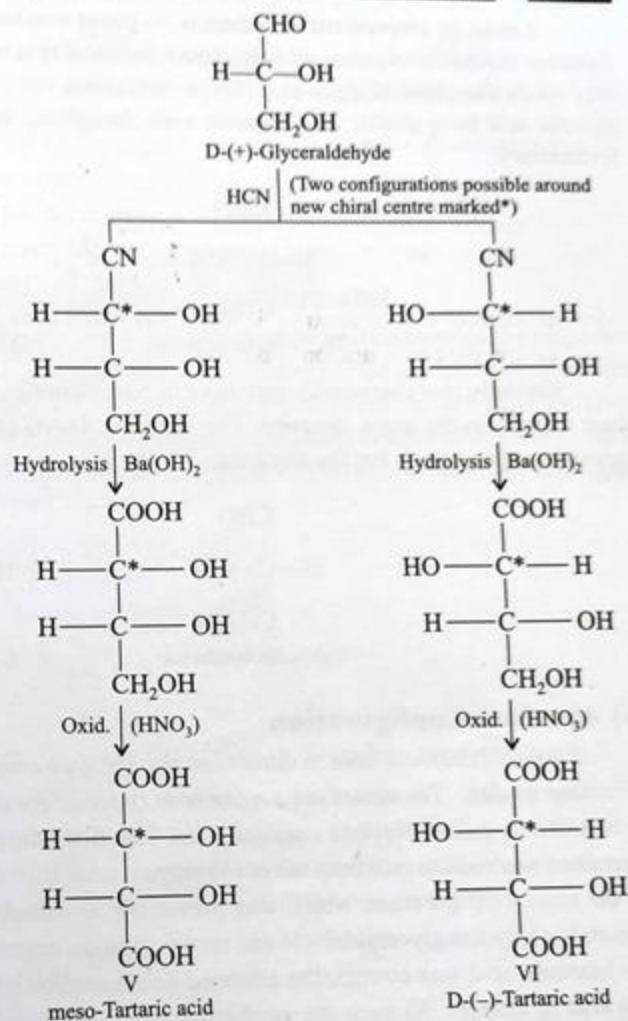


(ii) Configuration of (+)-Lactic Acid: The configuration of (+)-lactic acid was established to be similar to that of L-(-)-glyceraldehyde by the following reactions:

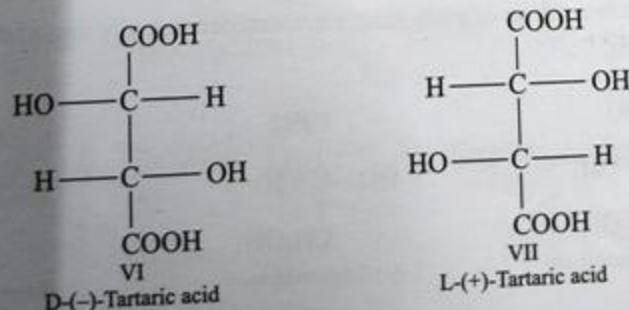


(iii) Configuration of

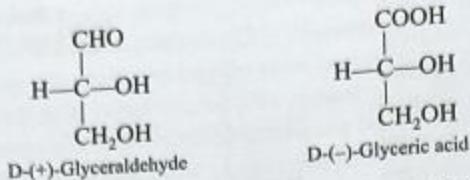
Tartaric Acid: When D-(+)-glyceraldehyde was converted into tartaric acid by the series of reactions shown, a mixture of two products was obtained. These two products differ from each other in their configuration around newly created chiral centre (marked *). One of the products was the inactive or mesotartaric acid (V). The other was the optically active tartaric acid which rotated the plane of light to the left i.e., it was (-)-tartaric acid. Since it was obtained from D-glyceraldehyde by reactions which did not involve breaking of bonds around the original chiral centre, it was assigned D-configuration i.e., the same as that of starting glyceraldehyde.



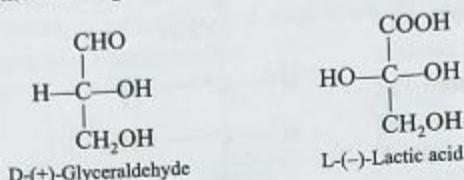
Since D-(-) tartaric acid was assigned configuration VI. L-(+) tartaric acid would naturally have the mirror image configuration, i.e., VII.



It must be emphasized that there is no direct relationship between absolute configuration and direction of rotation of polarised light. Two substances may have similar relative configurations and yet may rotate the plane of light in different directions. For example, D-(+)-glyceraldehyde and D-(-) glyceric acid have similar configuration even though the former is dextrorotatory while the latter is levorotatory.



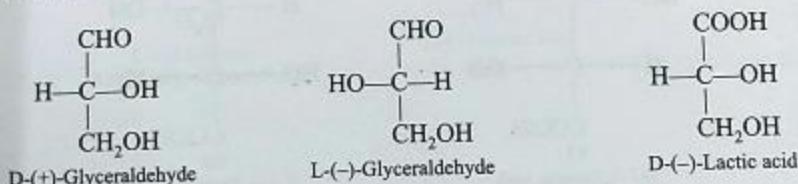
Similarly two compounds may have different configurations and even then they may rotate the plane of light in the same direction. For example, D-(+)-glyceraldehyde and L-(+)-lactic acid have opposite configurations but the same sign of rotation.



(B) Absolute Configuration

Bijvoet (1951) was able to determine the absolute configuration of a compound by using X-ray diffraction studies. The actual arrangement in space of the atoms or groups constituting a particular stereoisomer is called absolute configuration. The first compound whose absolute configuration was determined was sodium rubidium salt of (+)-tartaric acid. Bijvoet confirmed that (+)-tartaric acid actually has the same configuration, which was previously assumed to have on the basis of configurational relationship between glyceraldehyde and tartaric acid (as described earlier). If the assumed configuration of (+)-tartaric acid was correct, the assumed configuration of the two enantiomers of glyceraldehyde must also be correct. As such the configuration of all other compounds derived by correlation with glyceraldehydes must be correct ones. Thus the relative configuration assigned to D-(-)-glyceric acid, L-(-)-lactic acid (discussed earlier), carbohydrates and a large number of other compounds actually represent their absolute configuration.

The absolute configurations of some simple but stereochemically important compounds are given below in the planar form:



Module5-13- conf Alkane

Conformation of Alkane

5) 10.12 CONFORMATION OF ALKANES

Rotation around carbon-carbon single bond. Single covalent bond (σ bond) present between two carbon atoms is formed by the overlap of their sp^3 hybrid orbitals along the inter-nuclear axis. The electron distribution of the molecular orbital, thus formed, is cylindrically symmetrical around the axis of the bond. *Due to the axial symmetry of the molecular orbital, rotation around the C—C bond is almost free.* As a result of this rotation, alkanes can have different spatial arrangements, i.e. different relative arrangement of their atoms in space.

Such different spatial arrangements of atoms or groups of atoms in a molecule that can be readily inter-converted by rotation around C-C single bond are called conformers. They are rotational isomers and the phenomenon is called, conformational isomerism. The molecular geometry corresponding to a conformer is known as conformation.

10.12.1 Conformation of Ethane

In ethane molecule, if it is supposed that the position of one of the carbon atoms is kept fixed and the other is rotated about it, a large number of arrangements of the hydrogen of the carbon with respect to the hydrogen of the other can be obtained. Out of the infinite number of possible conformations of ethane, two conformations represent the extremes, as shown in Fig. 10.9. These are:

1. Eclipsed conformation
2. Staggered conformation.

- Eclipsed conformation:** In this conformation, the tetrahedrally attached three hydrogen atoms to front carbon are exactly in front of those attached to the back carbon, i.e., hydrogen atoms of both the carbon atoms are crowded together.
- Staggered conformation:** In this conformation, the tetrahedrally attached hydrogen atoms to two carbon atoms are as far apart as possible. It is important to note the basic structure of the molecule and the various bond lengths and bond angles remain the same in both the conformations. These are called **Sawhorse method** of representing the conformations. (Fig. 10.9).

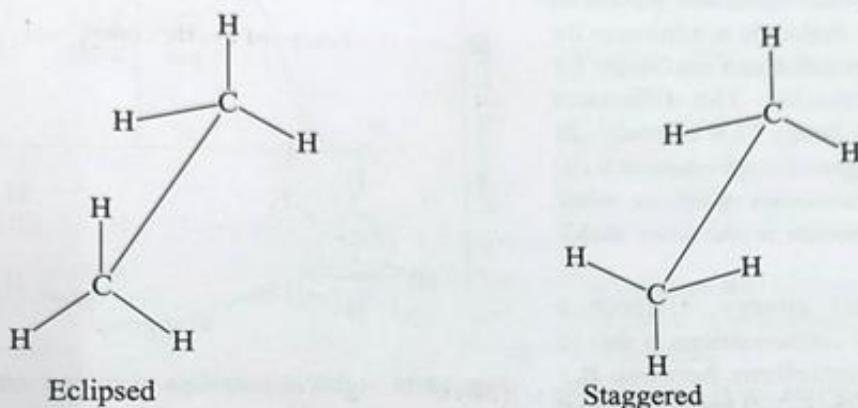


Fig. 10.9 Eclipsed and staggered conformations of Ethane

Newman's style of representing the conformations of molecules is more popular. Thus the two conformations of ethane may be represented by **Newman's projections** as shown in Fig. 10.10.

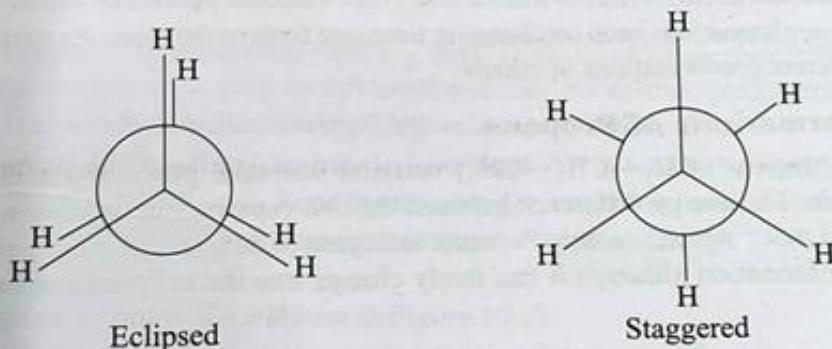


Fig. 10.10 Newmen's projection for the conformations of Ethane.

In Newman projection, the two carbons forming a bond are represented by two circles, one behind the other, so that only the front carbon is seen. The hydrogen atoms attached to the front carbon are depicted by C—H bonds from the centre of the circle. The C—H bonds of the back carbon are drawn from the circumference of the circle.

One conformation of ethane gets converted into the other when rotated through an angle of 60° .

Relative Stabilities of Conformations of Ethane

It must be pointed out here that rotation around the single bond is *not completely free*. If it were so, the potential energy of different conformations should have been the same. But in actual practice, the potential energy of the molecule changes somewhat with the rotation around C—C single bond. Thus the potential energy of ethane molecule is minimum for staggered conformation and maximum for eclipsed conformation. The difference between the two being 12.6 kJ mol⁻¹. In other words, *staggered conformation is the most stable conformation of ethane while eclipsed conformation is the least stable* (Fig. 10.11).

The small energy difference between different conformations is due to the repulsive interactions between the electron clouds of the C—H bonds attached to the central C—C bond. In the staggered conformation of ethane, the electron clouds of these carbon hydrogen bonds are as far apart as possible. But in the eclipsed conformation, the three C—H bonds of one carbon are closest to the three C—H bonds of the other carbon. The repulsive interactions between the electron clouds in this position increase the energy of the molecule and thus decrease its stability.

But the energy difference is not large enough to prevent rotation. Even at ordinary temperature, the molecules possess sufficient thermal or kinetic energy to overcome the energy barrier through effective collisions and thus conformations keep on changing from one form to the other. As such it is not possible to separate the different conformations of ethane.

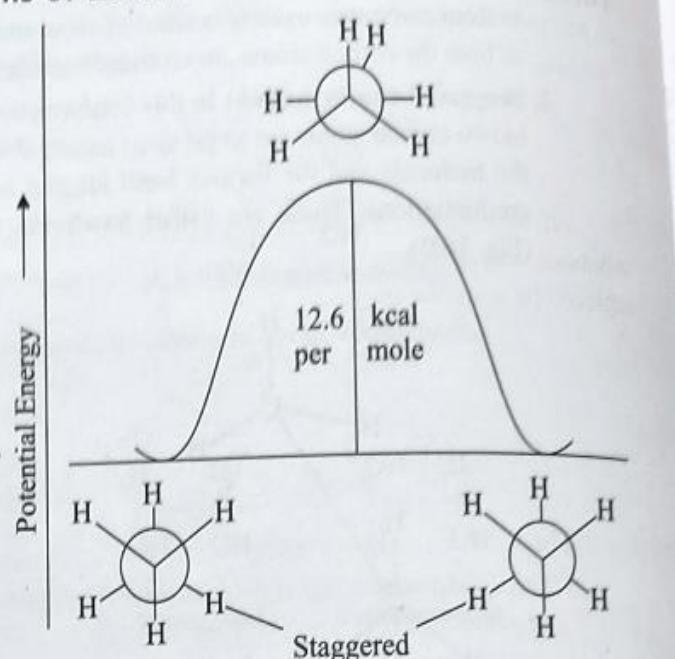


Fig. 10.11 Relative stabilities of conformations of Ethane

10.12.2 Conformations of Propane

In case of propane ($\text{CH}_3\text{—CH}_2\text{—CH}_3$) rotation can take place about either of the two carbon-carbon bonds. The energy difference between the two extreme conformations *i.e.* eclipsed and staggered, is 13.8 kJ mol^{-1} which is nearly the same as in case of ethane. The most stable conformation is the staggered conformation although it can freely change into the eclipsed conformation and vice versa.

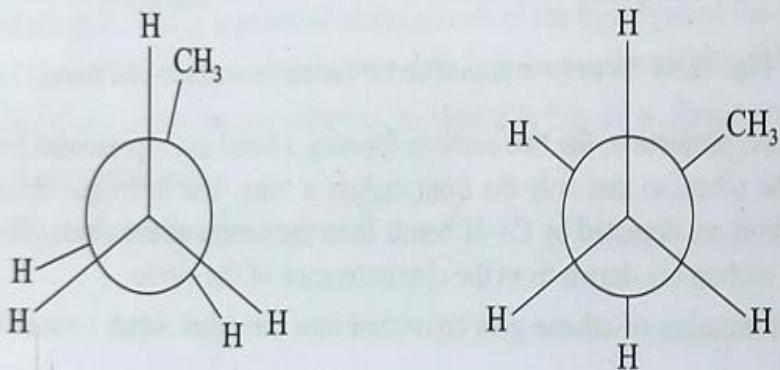
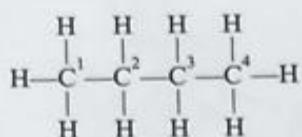
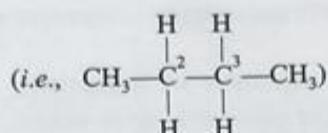


Fig. 10.12 Newman's projections for the conformations of propane.

10.12.3 Conformations of *n*-Butane



If we consider the rotation around the single bond between two carbon atoms (C_2 and C_3) of *n*-butane, we see that molecule is similar to ethane except that one hydrogen on each carbon has been replaced by a methyl group

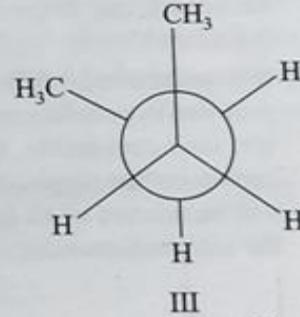
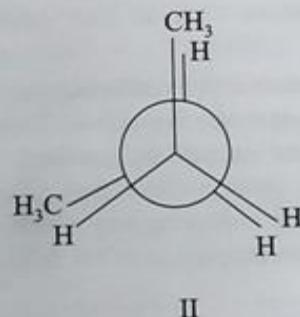
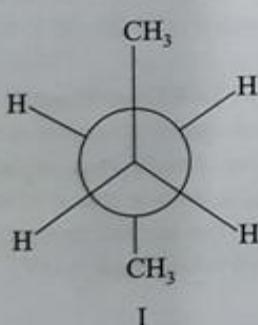


The various possible conformations of *n*-butane are:

- (i) **Anti conformation (I):** In this conformation, methyl groups and hydrogen linked to two carbon atoms (C_2 and C_3) are at a maximum distance apart. It is assumed that the angle of rotation around the $\text{C}_2 - \text{C}_3$ bond is zero for this conformation.
- (ii) **Eclipsed conformation:** Starting from the anti conformation, if we rotate the $\text{C}_2 - \text{C}_3$ single bond through 60° , we get the partially eclipsed form II. In this conformation, the methyl group attached to one carbon atom is at the back of hydrogen atom (rather than the methyl group) attached to the other carbon atoms.
- (iii) **Gauche or skew configuration:** On rotating $\text{C}_2 - \text{C}_3$ single bond by another 60° , we get the staggered conformation III is also known as gauche or skew form. In this conformation, the various bonds are farthest apart but the methyl groups make an angle of 60° with respect to each other.
- (iv) **Fully eclipsed conformation:** Rotating the $\text{C}_2 - \text{C}_3$ bond by another 60° gives rise to fully eclipsed conformation (IV). In this conformation, the methyl groups and hydrogen atoms attached to two carbon atoms completely eclipse each other.

Further rotation of 60° gives rise to the gauche form (V) in which the methyl groups are again 60° apart. On further rotating $\text{C}_2 - \text{C}_3$ bond by 60° , we get another eclipsed conformation (VI). Still further rotation of $\text{C}_2 - \text{C}_3$ by 60° and thus completing the rotation through 360° , we get antiform (I) again.

The various conformations are shown in Figure 10.13.



(Fig. contd...)

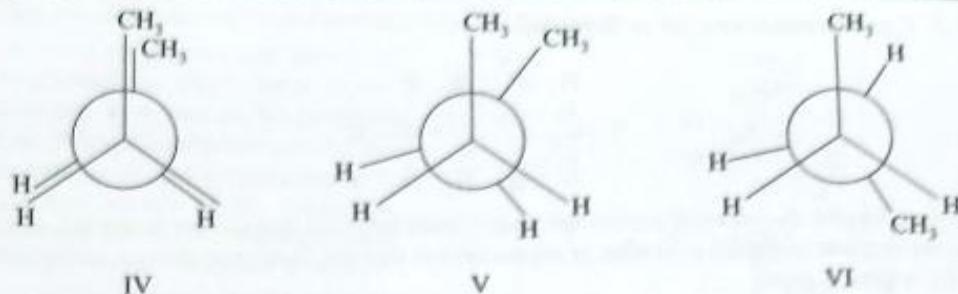
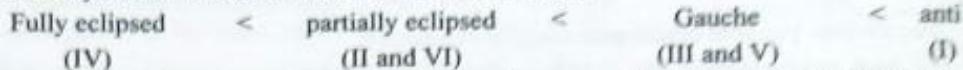


Fig. 10.13 Newman's projection for the conformations of *n*-butane

Relative Stabilities of Conformations of *n*-Butane

The stability of conformations of *n*-butane is in the order:



- (i) In fully eclipsed conformation IV, there is maximum repulsion between the bonding electrons and bulky methyl group. Repulsion between bonding electrons produces *torsional strain* in the conformation while the crowding together of the bulky methyl group causes *steric or Van der Wall's strain* in the molecule. Due to torsional strain and steric strain, this conformation has maximum energy and minimum stability.
- (ii) In the partially eclipsed conformation (II and VI) the repulsive interaction between the bulky methyl group and bonding electrons is less than in fully eclipsed conformation (IV). Thus, *partially eclipsed conformations are more stable than fully eclipsed conformation*.
- (iii) In gauche conformation (III and V) there are weak repulsive interactions between two methyl groups as they are 60° apart. In other words, there is a slight Van der Wall's strain but no torsional strain. Thus, *it is more stable than partially eclipsed conformation*.
- (iv) In anti conformation (I), the repulsive interaction between the two methyl groups and bonding electrons is minimum because the two methyl groups are maximum distance apart. Thus, *this conformation is free of torsional as well as steric strain*. Hence it is the **most stable conformation**.
- (v) As anti conformation and Gauche conformations have staggered arrangements, they have maximum energy and maximum stability (anti conformation is slightly more stable than Gauche conformation). **These conformations are referred to as conformational isomers.**
- (vi) The difference in energy contents between conformations I and IV is about 18.4 kJ mol^{-1} , between I and II (or VI) is about 14.6 kJ mol^{-1} and between I and III or V is only 3.8 kJ mol^{-1} .
- (vii) Maximum energy difference between two conformations is only 18.4 kJ/mol which is easily provided by colliding molecules at room temperature. Thus various conformations of *n*-butane are inter-convertible and hence cannot be isolated. In other words rotation around carbon-carbon single bond in *n*-butane is almost free. At any time, *n*-Butane at an equilibrium will be mixture of all the possible conformations which contains the highest percentage of the anti conformation(s) and least proportion of the fully eclipsed conformation (IV).

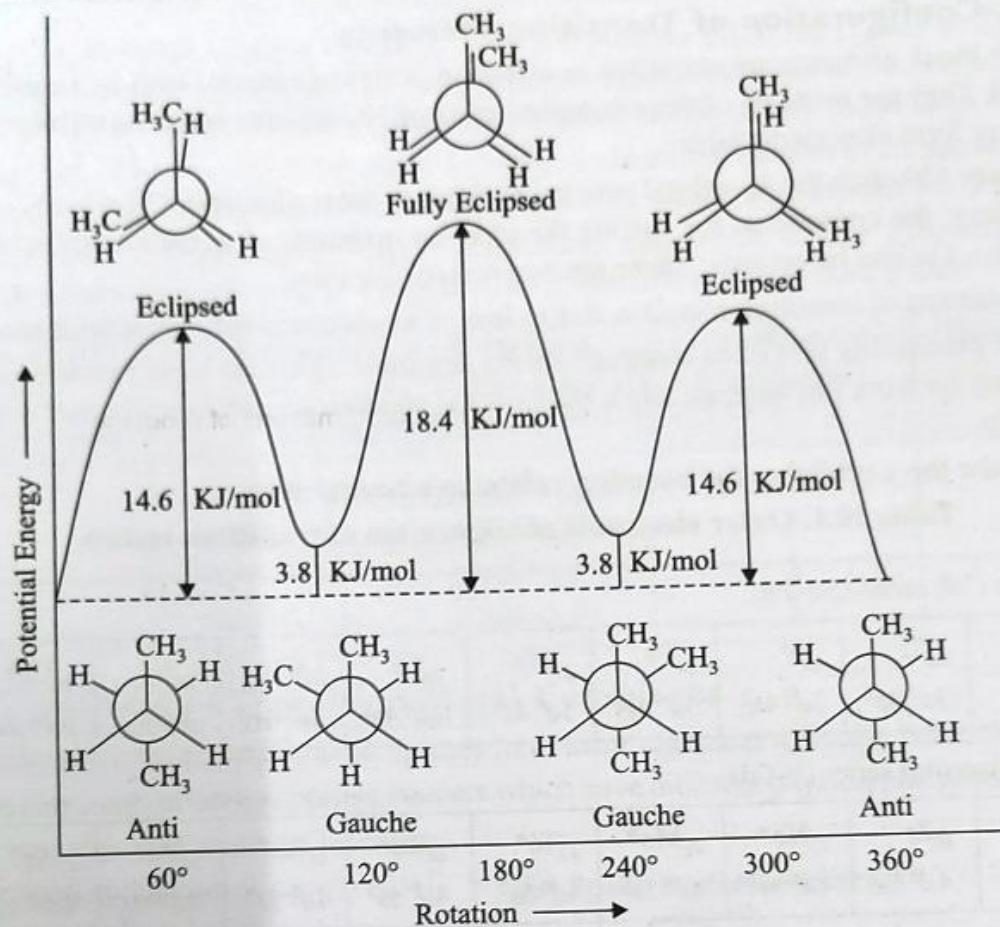


Fig. 10.14 Energy Changes during rotation around the carbon-carbon bond in n-Butane

Module5-14-stereo ques

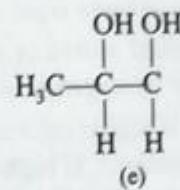
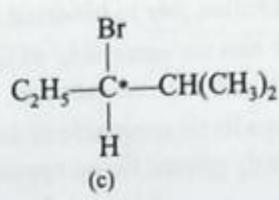
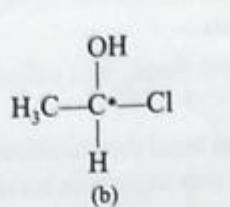
Stereochemistry Question

PROBLEM WITH SOLUTIONS

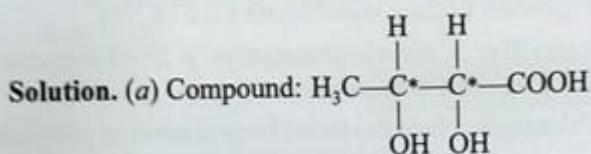
Problem 1. Which of the following compounds will exhibit optical isomerism:

- (a) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ (b) $\text{CH}_3\text{CH}(\text{OH})\text{Cl}$
(c) $\text{CH}_3\text{CH}_3\text{CH}(\text{Br})\text{CH}_3(\text{CH}_3)_2$ (d) $\text{CH}_2(\text{Cl})\text{CH}_2\text{OH}$
(e) $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_3$

Solution. Compounds (b), (c) and (e), because they contain chiral (or asymmetric) carbon atom or atoms.

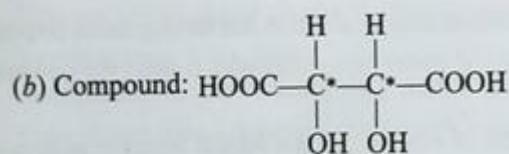


Problem 2. Mark the asymmetric carbon atoms and give the number of optical isomers in the following compounds:



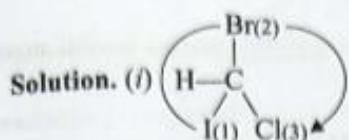
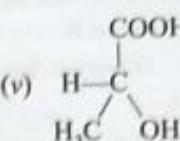
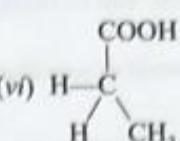
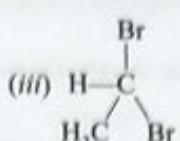
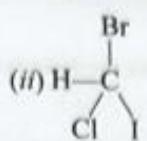
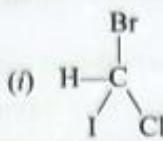
Contains two asymmetric carbon atoms.

Therefore, number of optical (*d*- and *l*) isomers $- 2^2 = 4$.



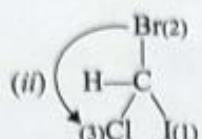
Contains two asymmetric carbon atoms, but it can be divided into two equal halves, so number of optical isomers $= 2^2 - 1 = 3$.

Problem 3. Assign R and S configuration for each of the following compounds:



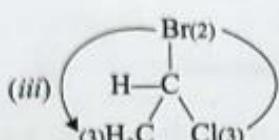
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∴ R (Clockwise)



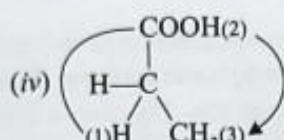
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∴ S (Anti-clockwise)



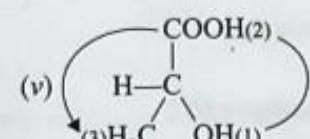
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∴ S (Anti-clockwise)



← Viewer

∴ R (Clockwise)



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∴ S (Anti-clockwise)

Problem 4. What is the necessary and sufficient condition for a molecule to be optically active?

Solution. The necessary and sufficient Condition for a molecule to be optically active is that its molecule should be chiral, i.e., the molecule and its mirror image should be non super-imposable.

Problem 5. Does the presence of one chiral carbon atom make the molecule optically active? Explain.

Solution. Yes. The presence of one chiral C-atom in a molecule always makes it chiral and hence shows optically activity.

Problem 6. Does the presence of two chiral carbon atoms always make the molecule optically active? Explain.

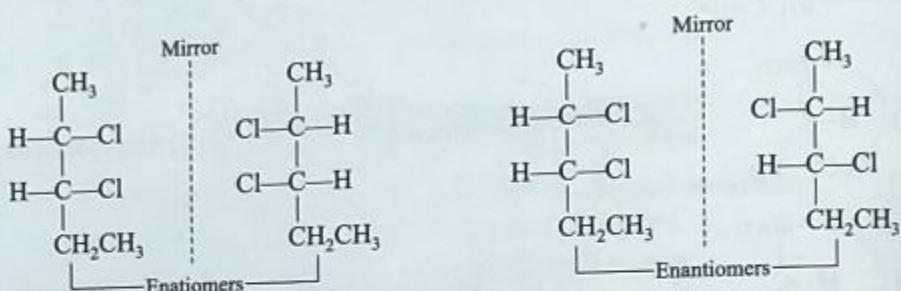
Solution. Not necessarily. The presence of two similar chiral carbon atoms may or may not make the molecule optically active. If the molecule as a whole is chiral; it is optically active and if the molecule as a whole is achiral, it is optically inactive. For example, (+)-tartaric acid, and (-)-tartaric acid are optically active because their molecules are chiral. i.e. the molecules and their respective mirror image

are non-superimposable. On the other hand, meso-tartaric acid is optically inactive because its molecule is achiral, i.e. the molecule and its mirror image are superimposable due to the presence of a plane of symmetry in it.

However, the presence of two dissimilar chiral carbon atoms always makes the molecule optically active.

Problem 7. How many pairs of enantiomers are possible for the compound, 2, 3-dichloropentane? Explain.

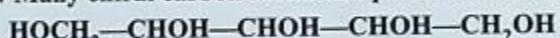
Solution. Two pairs of enantiomers, i.e. four optically active forms of 2, 3-dichloropentane are possible. These are



Problem 8. Does the absence of chiral carbon atoms, always make a molecule optically inactive? Explain.

Solution. Not necessarily. A molecule is optically active if it is non-superimposable on its mirror image. It may or may not contain chiral carbon atoms. For example, 6, 6'-dinitrodiphenic acid and Penta-2, 3-diene are optically active even though, they, do not contain chiral carbon atoms. The reason being that these molecules are chiral, i.e., the molecules and their respective mirror images are non-superimposable.

Problem 9. How Many chiral carbon atoms are present in the molecule,



and how many optically active stereoisomer are possible for this compound?

Solution. The compound,



contains only two similar chiral carbon atoms as marked by asterisks. The middle carbon atom is symmetrically substituted and hence is not chiral. Therefore, like tartaric acid, it also exists in three stereo-isomeric forms, i.e. (+), (-) and meso.

Problem 10. Which of the following compounds would show optical isomerism :

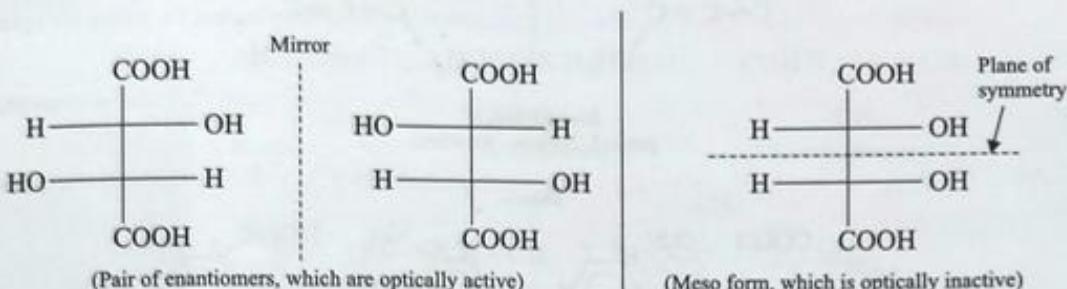
- | | |
|--|---|
| (i) $\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{COOH}$ | (ii) $(\text{CH}_3)_2\text{CH} \cdot \text{CHO}$ |
| (iii) $\text{H}_2\text{N} \cdot \text{CH} \cdot (\text{CH}_3)_2$ | (iv) $\text{CH}_3-\overset{*}{\text{CH}}(\text{OH})\text{COOH}$ |



Solution. (iv) $\text{H}_3\text{C}-\overset{*}{\text{C}}-\text{OH}$, will show optical isomerism, as it possesses chiral carbon atom, marked with asterisk*.

Problem 11. Discuss stereochemistry of tartaric acid.

Solution. Different configurations of tartaric acid are as under:



Thus, there are three forms of tartaric shown above.

(i) Dextro or + form of tartaric acid

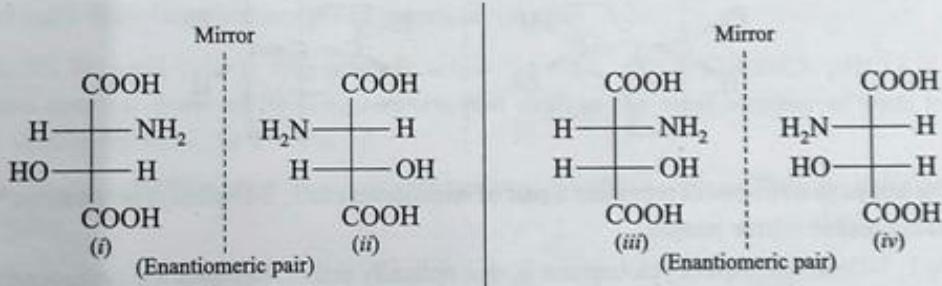
(ii) Laevo or - form of tartaric acid

(iii) Meso tartaric acid, which is optically inactive due to internal compensation.

There can be a racemic mixture (\pm tartaric acid), which contains (+) and (-) form in equal amounts. It is optically active due to external compensation.

Problem 12. What will happen if one of the OH groups of tartaric acid is replaced by NH_2 group?

Solution. If one of the OH groups of tartaric acid is replaced by NH_2 group, possible configuration will be

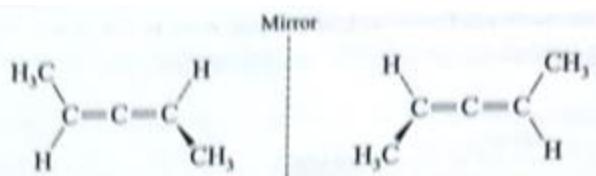


Thus, number of optically active forms will increase. Beside the above four forms there are diasteroids. Structure (iii) is diasteroid of structure (i). Similarly structure (iv) is diasteroid of structure (ii) and so on.

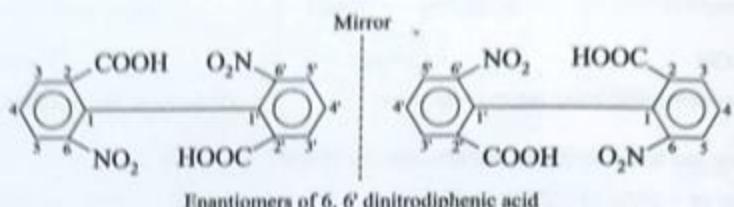
Problem 13. Give examples of optically active compounds without chirality,

Solution. There are many compounds which do not contain chiral carbon atoms but their molecules are chiral or dissymmetric and hence show enantiomerism or optical activity.

For example, allenes and o-substituted diphenyls do not contain chiral carbon atoms but their molecules are non-superimposable on their respective mirror images and hence show enantiomerism or optical activity.



Enantiomers of
penta-2, 3-diene - An allene



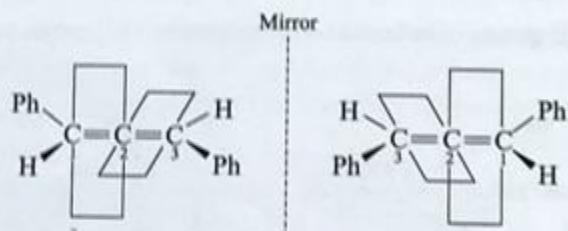
Enantiomers of 6, 6' dinitrodiphenic acid

Problem 14. The following compounds are optically active or not? Explain.

(a) 1, 3-Diphenyl propadiene

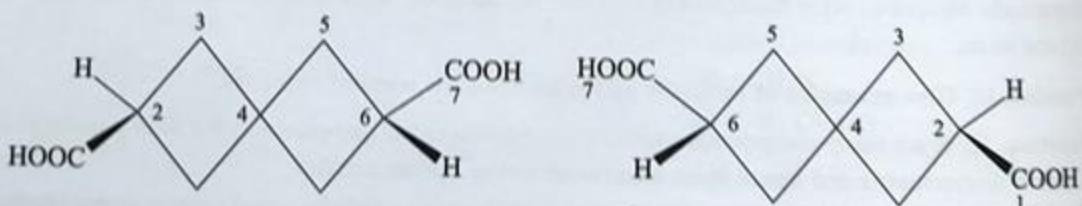
(b) 1, 7-Dicarboxylspirocycloheptane

Solution. (a) 1, 3-Diphenyl propadiene is optically active, because its structure shown below confirms it to be a dissymmetric molecule.



The above two structures represent a pair of enantiomers of 1, 3-Diphenyl propadiene, which are non-superimposable mirror images.

(b) 1, 7-Dicarboxylspirocycloheptane is also optically active. Spiranes are compounds having a carbon atom common to rings. The two rings are perpendicular to each other. Spiranes exhibit optical isomerism because of restricted rotation as shown below.



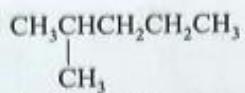
The above two configurations represent a pair of enantiomers of 1, 7-Dicarboxyl spirocycloheptane, which are non-superimposable mirror images.

Problem 15. Name the isomeric forms of C_6H_{14} according to the IUPAC system. Which one(s), if any, is (are) optically active?

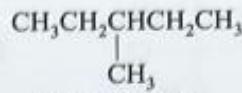
Solution.



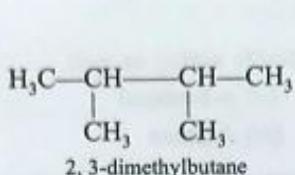
hexane



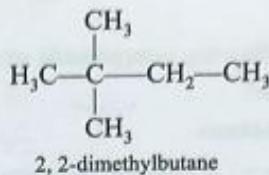
2-methylpentane



3-methylpentane



2, 3-dimethylbutane



2, 2-dimethylbutane

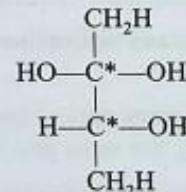
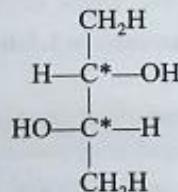
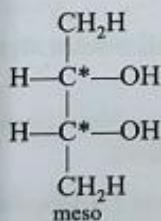
None of these isomers is optically active.

Problem 16. Explain the difference between a meso-isomer and a racemic mixture. What characteristic(s) do they have in compound?

Solution. A meso isomer is a single compound; a racemic mixture contains an equimolar mixture of two compounds. The meso isomer is inherently inactive because of internal compensation; the racemic mixture does not rotate the plane of polarized light because the effect of one of the isomers cancels the effect of the other. The racemic mixture can be separated into two optically active compounds by physical means. The meso isomer and the racemic mixture have in common their inability to rotate the plane of polarized light. Both have two centres of (opposite) chirality.

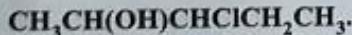
Problem 17. Tartaric acid is dihydroxydicarboxylic acid, $HOCOCHOHCHOHCO_2H$. Identify any chiral centres, draw all optical isomers, and explain the total number of such isomers of tartaric acid in terms of the 2^n rule.

Solution. The two middle carbon atoms in each structure are chiral centers. They are starred to indicate their chirality.



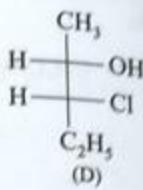
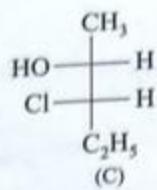
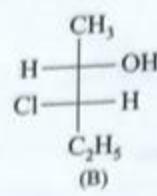
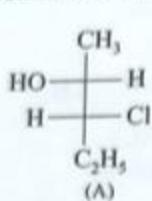
There are 3 isomers instead of $2^2 = 4$, one is a meso isomer.

Problem 18. (a) Draw all the stereoisomers of 3-chloro-2-pentanol,



(b) Give the stereochemical relationships of the stereoisomers.

Solution. (a) There are four stereoisomers. A and B are enantiomers, as are C and D (b) A and B are diastereomers of C and D.

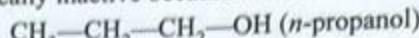


Problem 19. The following compounds are optically active or not:

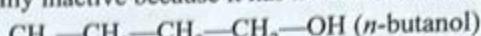
- (i) n-propanol
 (ii) n-butanol
 (iii) 2-chlorobutane

- (iv) Allenes

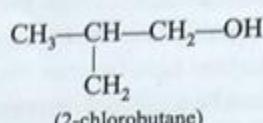
Solution. (i) n-propanol is optically inactive because it has no chiral carbon.



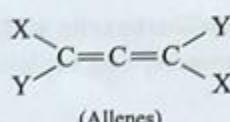
(ii) n-butanol is optically inactive because it has no chiral carbon.



(iii) 2-chlorobutane is optically active, because it has a chiral carbon.



(iv) Allenes are optically inactive because they do not contain any chiral carbon.



Problem 20. Are all optical isomers necessarily optically active? Explain

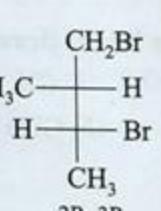
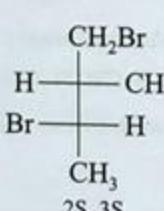
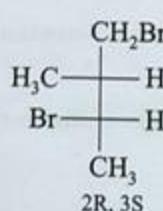
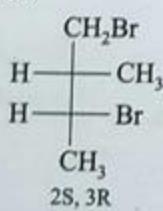
Solution. Meso isomers are optically inactive, despite being in the class of optical isomers.

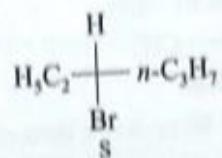
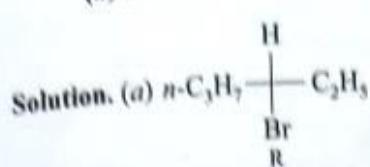
Problem 21. How many optical isomers can exist in 2,3-butanediol? Would all of these be optically active?

Solution. There are three optical isomers, one of which is inactive (the Meso form) because of the two carbon atoms having the same groups arranged in opposite configuration.

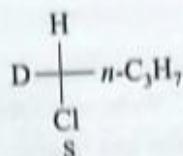
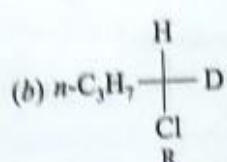
Problem 22. Give the R/S designation for each of the stereoisomers of 1,3-dibromo-2-methylbutane.

Solution. There are two chiral C's (C^2 and C^3), and the four stereoisomers are shown below with their designation.



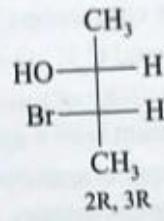
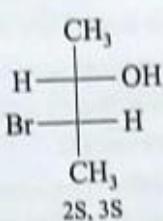
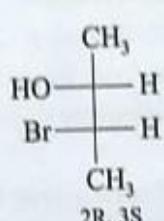
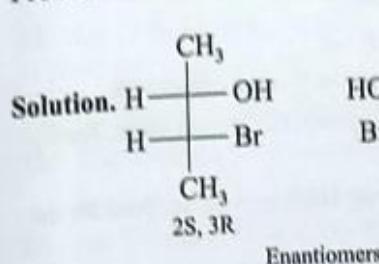


$$\text{Br} > \text{C}_1, \text{C}_2, \text{C}_3 > \text{C}_4, \text{C}_5, \text{H} > \text{H}_1$$



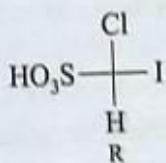
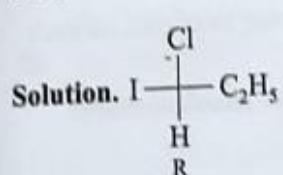
Cl > C > D > H

Problem 24. Draw stereochemical formula of $\text{CH}_3\text{CHBrCHOHCH}_3$ and give R/S designation.



Enantiomers

Problem 25. Draw the enantiomers of (a) chloriodomethane sulphonic acid and label each as R or S.



$$\text{I} > \text{Cl} > \text{S} > \text{H}_2$$