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# Syllabus

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## B.Sc. (Part I) Chemistry Chemistry-I : Inorganic Chemistry SC-107

### UNIT-I: ATOMIC STRUCTURE AND PERIODIC PROPERTIES

Dual nature of matter and idea of de Broglie matter waves, de Broglie equation; Wave mechanical model, Heisenberg uncertainty principle, Schrodinger wave equation (Derivation not required), Quantum numbers, Aufbau and Pauli exclusion principles. Hund's multiplicity rule.

Definitions and applications of atomic and ionic radii, ionization energy, electron affinity and electronegativity.

### UNIT-II : CHEMICAL BONDING

Valence bond theory and its limitations, various types of hybridization and shapes of simple inorganic molecules and ions. Ionic structures, radius ratio effect and co-ordination number, limitation of radius ratio rule, Fajan's rule, inert pair effect, singlet bond, odd electron bonds and hydrogen bond.

### UNIT-III : s-BLOCK AND p-BLOCK ELEMENTS

Comparative study, diagonal relationship, characteristics including their positions in the periodic table. Abnormal behaviour of Li and Be. Preparation, properties and uses of lithium aluminium hydride, Comparative study of groups 13-17 elements, characteristics including their positions in the periodic table, Preparation and properties of diborane, borax, sodium thiosulphate, interhalogens, freon and teflon.

### UNIT-IV : CHEMISTRY OF NOBLE GASES

History and isolation of noble gases, Position of noble gases in periodic table, compounds of noble gases.

### UNIT-V : RADIOACTIVITY

Disintegration theory, group displacement law, rate of disintegration, half life period, Average life period, disintegration series, radioactive equilibrium, artificial radioactivity, types of nuclear reactions, nuclear fission and fusion, applications of radioactivity.

### UNIT-VI : CHEMISTRY OF ELEMENTS OF FIRST SECOND AND THIRD TRANSITION SERIES

Characteristic properties of *d*-block elements.

Properties of the elements of the first transition series, their binary compounds and complexes illustrating relative stability of their oxidation states, coordination number and geometry.

General characteristics, comparative treatment with their 3-analogues in respect of ionic radii, oxidation states, magnetic behaviour, spectral properties and stereochemistry.

### UNIT -VII : COORDINATION COMPOUNDS

Werner's coordination theory and its experimental verification, effective atomic number concept, chelates, nomenclature of co-ordination compounds, isomerism in coordination compounds, valency bond theory, inner and outer orbital complexes

### UNIT-VIII : LANTHANIDES AND ACTINIDES

**Chemistry of lanthanides :** Occurrences, electronic structure, oxidation states, oxidation potential colour, solubility, colour, ionization potential, reactivity, melting and boiling points atomic and ionic radii, lanthanide contraction, complex formation, magnetic properties, separation of lanthanides.

**Chemistry of actinides :** General characteristics and chemistry of actinides, actinide contraction, Similarities between lanthanides and actinides, Chemistry of extraction of uranium,.

### UNIT-IX : GENERAL METHODS OF EXTRACTION, PURIFICATION OF METALS, AND METALLURGY

General methods of extraction and purification of metals, chemistry involved in the extraction of metals, e.g., titanium, vanadium, chromium, nickel and platinum.

### UNIT-X: STUDY OF COMPOUNDS:

Preparation, properties and uses of the following compounds : Titanium dioxide, titanium tetrachloride Chromyl chloride potassium dichromate, potassium permanganate, Potassium Ferrocyanide, potassium ferricyanide, chlorophatnic acid, sodium cobaltinitrite sodium nitro prusside

## 1

# ATOMIC STRUCTURE AND PERIODIC PROPERTIES

## STRUCTURE

- Dual Nature of Matter
- Wave Mechanical Model
- Heisenberg Uncertainty Principle
- Schrodinger Wave Equation
- Quantum Numbers
- Aufbau Principle
- Pauli's Exclusion Principle
- Hund's Rule of Maximum Multiplicity
- Atomic Radius
- Ionic Radius
- Ionic Radius
- Ionization Energy
- Electron Affinity
- Electronegativity
- Student Activity
- Summary
- Test Yourself

## LEARNING OBJECTIVES

After going this unit you will learn :

- The modern theory of the structure of the atom.
- Atomic orbital and different types of quantum number.
- The principles for filling up of the electrons in different orbitals.
- Covalent, vander Waal's and Crystal radii.
- Ionization energy, electron affinity and their applications in explaining the chemical behaviour.
- Electronegativity of the atom and its variation regarding a group and a period.

### 1.1. DUAL NATURE OF MATTER

Einstein (1905) suggested that light has a dual character and behaves both as a particle and as a wave. L. de Broglie (1924) suggested that all material particles in motion such as electrons, protons, neutrons, atoms, molecules etc. have dual character. According to L. de Broglie, any moving electron in the atom is a material particle associated with wave properties and he compared electrons with photons having negligible masses.

According to L. de Broglie, the wavelength  $\lambda$  of a particle of mass  $m$  and velocity  $u$  is given by the relation :

$$\lambda = \frac{h}{mu}$$

where  $h$  is Planck's constant and  $mu$  is the momentum of the particle.

**Derivation of de Broglie's equation :** The relation between the particle nature and wave nature of electron is known as de Broglie equation. According to Planck, the energy of a quantum of radiation is given by :

$$E = h\nu \quad \dots (i)$$

According to Einstein, mass and energy are related as :

$$E = mc^2 \quad \dots (ii)$$

where  $c$  is the velocity of light.

Combining equations (i) and (ii), we have :

$$h\nu = mc^2$$

or

$$\frac{h\nu}{c} = mc$$

or

$$\frac{h}{c/\nu} = mc$$

or

$$\frac{h}{\lambda} = mc$$

or

$$\lambda = \frac{h}{mc}$$

This equation is applicable for photon. According to L. de Broglie, the above equation can also be applied to material particles by substituting the mass of the particle  $m$  and its velocity  $u$  in place of velocity of light  $c$ . Thus, wavelength  $\lambda$  of material particle is given by

$$\lambda = \frac{h}{mu}$$

This relation is known as de Broglie equation.

or

$$\lambda = \frac{h}{p}$$

where  $p$  is the momentum of the particle. This helps us in the calculation of wavelengths of atom waves.

## • 1.2. WAVE MECHANICAL MODEL

The motion of electron in the atom is not simply mechanical as postulated by Bohr and Sommerfield. The modern theory of the structure of the atom is based upon wave mechanics given by de Broglie and Schrodinger. According to de Broglie, any moving electron in the atom is a material particle associated with wave properties. Instead of moving in a definite orbit, the electrons move in a random manner, sometimes close to the nucleus and sometimes a distance far away from it. It moves in all the directions instead of moving in one plane.

According to Bohr's theory, the electrons move in only those orbitals for which the angular momentum of the moving electron is an integral multiple of  $\frac{h}{2\pi}$  i.e.,

$$mvr = \frac{nh}{2\pi}$$

De Broglie equation helps to explain the Bohr's postulate of quantisation of angular momentum of an electron. Consider an electron moving around the nucleus in the form of a wave in a circular orbit of radius  $r$ . The electron wave may be continuously in phase or out of phase. If the circumference of the circular orbit is an integral multiple of wavelength, the electron wave is in phase [Fig. (1)] but if the circumference of the circular orbit is not an integral multiple of wavelength, the electron wave will go out of phase [Fig. (2)].

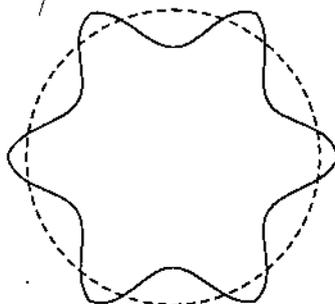


Fig. 1. Wave in phase.

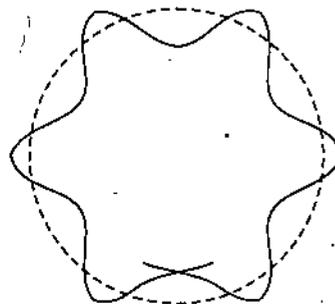


Fig. 2. Wave out of phase.

Thus, circumference =  $n\lambda$  or  $2\pi r = n\lambda$  ... (i)

But according to de Broglie equation,  $\lambda = \frac{h}{mu}$  ... (ii)

From equations (i) and (ii),  $2\pi r = \frac{nh}{mu}$  or  $mur = \frac{nh}{2\pi}$

Thus, the angular momentum of the moving electron should be an integral multiple of  $\frac{h}{2\pi}$ , or in other words, the angular momentum of the electron is quantised. This is Bohr's postulate which was given without any theoretical basis.

### • 1.3. HEISENBERG'S UNCERTAINTY PRINCIPLE

According to this principle,

*'It is impossible to determine simultaneously both the position and the velocity or momentum of a small moving particle like an electron.'*

The physical concept of the uncertainty principle may be clear by assuming that all observations have to be made by impact of light radiations or photons. If the object is of a reasonable bigger size, its position or velocity will not be changed by the impact of light photons. So, it will be possible to know both the position and velocity of the object. However, this is not possible when the object is very small, such as an electron. It will suffer a change in its path and velocity due to the impact of even a single photon of light. The path and velocity of an electron, after the impact of light photons, may be quite different from the original path and velocity.

On this basis, Bohr's model in which electrons are considered as particles revolving in definite orbits, *i.e.*, well-defined path, does not hold good. However, it will be more correct to say that an electron is associated with a certain energy, *i.e.*, it belongs to a definite energy level and not that it belongs to a definite orbit.

**Uncertainty and concept of probability :** As seen above, it is not possible to know exactly both the position and the momentum of an electron. Thus, certainty of determination of one property introduces uncertainty of determination of the other. The uncertainty in measurement of position,  $\Delta x$ , and the uncertainty of determination of momentum,  $\Delta p$  are related by Heisenberg's relationship as

$$(\Delta x) \times (\Delta p) \geq \frac{h}{4\pi}$$

where  $h$  is Planck's constant.

If  $\Delta x$  is very small, *i.e.*, the position of the electron is known more or less exactly,  $\Delta p$  would be large, *i.e.*, uncertainty with regard to momentum will be large or vice-versa.

On the basis of concept of probability, it is possible to state or predict the probability or relative chance of finding an electron of a particular energy in a given region of space at a given time. The volume in space around the nucleus of the atom, in which there is maximum probability of finding an electron, is called an *orbital*.

### • 1.4. SCHRODINGER WAVE EQUATION

Starting from de Broglie's concept, Schrodinger developed the theory of wave mechanics and obtained a mathematical equation describing the state of an electron in terms of mass ( $m$ ), total energy ( $E$ ), potential energy ( $V$ ) relative to atomic nucleus, Planck's constant ( $h$ ) and a quantity  $\psi$  called the wavefunction of the electron (or the amplitude of the wave). The equation is called Schrodinger's wave equation. It can be developed from the general differential equation of wave motion in one dimension, *i.e.*, along X-axis.

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

where  $h$  is Planck's constant and  $\psi$  is wavefunction.

**Significance of wave function,  $\psi$ .** The wave function,  $\psi$  in Schrodinger equation has no physical significance except that it shows the amplitude of the electron wave. The value of  $\psi^2$  gives the probability of finding an electron of a given energy,  $E$ , from place to place in a given region around the nucleus.

It is possible to identify region of space around the nucleus where there is a high probability of finding an electron associated with a certain energy. The space is known as an *atomic orbital*.

It may be noted that in Bohr's theory, the electron associated with a certain energy is supposed to be situated at a certain distance from the nucleus. In wave mechanics, the equation for calculating the exact energy of the electron has been derived, but there is great uncertainty in finding its exact position. This is in conformity with Heisenberg's uncertainty principle.

## • 1.5. QUANTUM NUMBERS

An electron in an atom has some location relative to the nucleus and is associated with some energy. These properties describe the state of an electron in the atom. Various states, that are available to an electron, are governed by the laws of quantum mechanics. Thus, the numbers used to identify these states are known as *quantum numbers*. They specify the location and the energy of an electron. These are as follows :

**(1) Principal quantum number ( $n$ ) :** It gives the principal energy level to which the electron belongs. It specifies the location and energy of an electron. It may have any integral value, except zero. Thus,  $n$  will be equal to 1, 2, 3, ... depending upon whether the electron is in the first, second, third, ... (i.e., K, L, M, ...) principal energy levels. The maximum number of electrons in K, L, M, ... orbits can be 2, 8, 18, ... etc.

**(2) Angular momentum quantum number ( $l$ ) :** It is also known as *azimuthal quantum number* or *subsidiary quantum number*. It gives the energy position of an electron. i.e., this quantum number determines the energy associated with the angular momentum of the electron. It thus accounts for the appearance of a group of closely spaced spectral lines in the spectrum of hydrogen atom or hydrogen like atoms. Higher the value of this quantum number, greater will be the angular momentum of the electron. An electron having an angular momentum must have kinetic energy of angular motion. Therefore, the amount of angular kinetic energy must be well within the total energy of an electron given by the principal quantum number, i.e.,  $n$ . So, the possible integral values of  $l$  vary between 0 and  $(n - 1)$ .

If  $n = 1$ , then  $l$  can have only one value equal to zero, i.e.,  $l = 0$ . If  $n = 2$ , then  $l$  can have two values, i.e.,  $l = 0, 1$ . Similarly, if  $n = 3$ , the values of  $l$  will be 0, 1, 2 and if  $n = 4$ , the values of  $l$  will be 0, 1, 2 and 3.

If  $n$  gives the major energy level or shell,  $l$  gives the possible sub-levels or sub-shells within the same major energy level. The various sub-shells are designated by  $s, p, d, f$  depending upon the values of  $l$ . Therefore, when  $l = 0, 1, 2, 3, \dots$ , the sub-shells are designated by  $s, p, d, f, \dots$  respectively.

**(3) Magnetic quantum number ( $m$ ) :** It is well known that angular motion creates a magnetic field. Thus, angular momentum of electrons should create a magnetic field. This magnetism is determined by a quantum number called the *magnetic quantum number*.

Under the effect of magnetic field, the electrons in a given energy sub-shell prefer to orient themselves in certain definite regions of space around the nucleus. This region of space is called an *orbital* which represents well defined region in space where there is maximum probability of finding an electron of a particular energy. It is also called the *orientation quantum number*, because it gives the orientation or distribution of the electron cloud. The values of  $m$  depend upon the angular momentum quantum number,  $l$ . As is known from theory as well as experiment, the values of  $m$  may assume all the integral values between  $+l$  and  $-l$  through zero. It thus makes a total of  $(2l + 1)$  values.

(i) If  $l = 0$ , i.e., the sub-shell is  $s$ , then  $m$  can have only one value, 0. It means that  $s$ -sub-shell can have only one orbital viz., the  $s$ -orbital. Thus, there can be one possible orientation of electrons in space.

(ii) If  $l = 1$ , i.e., the sub-shell is  $p$ , then  $m$  can have three values, i.e.,  $m = -1, 0, +1$ . It means that  $p$ -sub-shell can have three orbitals, i.e., there can be three possible orientations of electrons in space.

(iii) If  $l = 2$ , i.e., the sub-shell is  $d$ , then  $m$  can have five values, i.e.,  $m = -2, -1, 0, +1, +2$ . It means that  $d$ -sub-shell can have five orbitals, i.e., there can be five possible orientations of electrons in space.

(iv) If  $l = 3$ , i.e., the sub-shell is  $f$ , then  $m$  can have seven values, i.e.,  $m = -3, -2, -1, 0, +1, +2, +3$ . It means that  $f$ -sub-shell can have seven orbitals, i.e., there can be seven possible orientations of electrons in space.

**(4) Spin quantum number ( $s$ ) :** This quantum number has been introduced due to the spectral evidence that an electron in its motion around the nucleus also rotates or spins about its own axis. Since an electron can spin clockwise or anti-clockwise (in two opposite directions), there are two possible values of  $s$  that are equal and opposite. As quantum numbers can differ only by unity from one another, there are two values given to  $s$ ,  $+1/2$  and  $-1/2$ , depending upon whether the electron spins in one direction or the other. These spins are designated by  $\uparrow$  and  $\downarrow$ . Two electrons having the same sign of the spin quantum numbers are said to have *parallel spins*, while those having opposite signs of the spin quantum numbers are said to have *opposite spins*, *antiparallel spins* or *paired up spins*.

## • 1.6. AUFBAU PRINCIPLE

As we pass from one element to another one of next higher atomic number, one electron is added every time to the atom. The principles involved in filling up of the electrons in different orbitals are as follows :

(i) The maximum number of electrons in any orbit or shell is  $2n^2$ , where  $n$  is the principal quantum number or number of the orbit.

(ii) The maximum number of electrons in a sub-shell ( $s, p, d$  or  $f$ ) is equal to  $2(2l + 1)$ , where  $l = 0, 1, 2$  or  $3$  ( $l =$  azimuthal quantum number). Thus, these sub-shells can have a maximum of 2, 6, 10 and 14 electrons, respectively.

(iii) Orbitals are filled up in order of their increasing energy. In other words, the orbital with a lower energy is filled up first before the filling of the orbital with a higher energy starts. As a working rule, a new electron enters the orbital where  $(n + l)$  is minimum. When  $(n + l)$  has the same value for two or more orbitals, the new electron enters the orbital where  $n$  is minimum. This is known as *aufbau principle* (German : aufbau = building up), i.e., the electrons are first accommodated in the orbitals of lowest energy.

$(n + l)$  values for various orbitals are given below :

$(n + l)$	1	2	3	4	5	6	7	8
Orbitals	1s	2s	2p	3p	3d	4d	4f	5f
			3s	4s	4p	5p	5d	6d
					5s	6s	6p	7p
							7s	8s

Using this rule, the most usual sequence in which the electrons occupy various orbitals is seen to be 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, 8s, etc.

An exception to this rule occurs where a single 5d electron is added before any 4f orbital is occupied. The remaining nine 5d electrons enter this sub-shell after the 4f sub-shell has been completely filled with 14 electrons. Similarly, one or more electron enters the 6d sub-shell before any electron occupies the 5f-sub-shell. This is because 4f and 5d sub-shells of energy are very close to each other and because 5f and 6d sub-shells are closer still.

(iv) There can be one  $s$ -orbital, three  $p$ -orbitals, five  $d$ -orbitals and seven  $f$ -orbitals. Each one of these orbitals can hold only two electrons with spins of  $+1/2$  and  $-1/2$ .

(v) Electron pairing in any  $s, p, d,$  or  $f$  orbitals is not possible until all the available orbitals of a given set contain one electron each. This is known as *Hund's rule of maximum multiplicity*.

(vi) Electrons tend to enter those sub-shells which, thereby, get either completely filled or exactly half-filled.

## • 1.7. PAULI'S EXCLUSION PRINCIPLE

The four quantum numbers viz., principal quantum number ( $n$ ), azimuthal quantum number ( $l$ ), magnetic quantum number ( $m$ ) and spin quantum number ( $s$ ), define completely the position of an electron in an atom. They represent the position of electron in the major energy level ( $n$ ), sub-energy level ( $l$ ), orientation in sub-energy level ( $m$ ) and the direction of the spin ( $s$ ). Thus, simply by stating the four quantum numbers, it is possible to identify an electron in an atom completely. This is because *no two electrons in a given atom can have the same four quantum numbers*. This fact is based on the important statement known as Pauli's exclusion principle. According to this principle,

*'It is impossible for any two electrons in the same atom to have all the four quantum numbers the same'.*

This principle is very useful in determining the maximum number of electrons that can exist in any quantum group, i.e., shells and sub-shells. For  $K$ -orbit,  $n = 1$ . Now  $l$  can have only one value ( $= 0$ ) and  $m$  can also have one value ( $= 0$ ). Hence,  $s$  can be either  $+1/2$  or  $-1/2$ . Thus, the two possibilities are :

$$\begin{array}{llll} n = 1 & l = 0 & m = 0 & s = +1/2 \\ n = 1 & l = 0 & m = 0 & s = -1/2 \end{array}$$

Thus, it means that in *K*-orbit, there is only one sub-shell  $l = 0$ , and in this only two electrons of opposite spins can be accommodated.

For *L*-orbit,  $n = 2$ . Now,  $l$  can have two values ( $= 0$  and  $1$ ),  $m$  can have three values ( $= -1, 0, +1$ ) and  $s$  can have two values ( $= +1/2, -1/2$ ). These possibilities give rise to the following eight combinations of the four quantum numbers, in the light of the exclusion principle.

$n = 2$	$l = 0$	$m = 0$	$s = +1/2$
$n = 2$	$l = 0$	$m = 0$	$s = -1/2$
$n = 2$	$l = 1$	$m = 0$	$s = +1/2$
$n = 2$	$l = 1$	$m = 0$	$s = -1/2$
$n = 2$	$l = 1$	$m = -1$	$s = +1/2$
$n = 2$	$l = 1$	$m = -1$	$s = -1/2$
$n = 2$	$l = 1$	$m = +1$	$s = +1/2$
$n = 2$	$l = 1$	$m = +1$	$s = -1/2$

Therefore, *L*-orbit can accommodate 8 electrons, 2 in the *s*-sub-shell ( $l = 0$ ) and 6 in the *p*-sub-shell ( $l = 1$ ).

Similarly, it can be seen that the maximum number of electrons in the *M*-orbit can be 18; 2 in the *s*-sub-shell ( $l = 0$ ), 6 in the *p*-sub-shell ( $l = 1$ ) and 10 in the *d*-sub-shell ( $l = 2$ ).

The Pauli's exclusion principle is of great importance in ascertaining the maximum number of electrons accommodated in any shell and sub-shell. The table shows the maximum number of electrons that can be accommodated in different shells and sub-shells.

Shell <i>n</i>	Sub-shells					Total number of electrons
	<i>s</i> -sub-shell ( $l = 0$ )	<i>p</i> -sub-shell ( $l = 1$ )	<i>d</i> -sub-shell ( $l = 2$ )	<i>f</i> -sub-shell ( $l = 3$ )	<i>g</i> -sub-shell ( $l = 4$ )	
1	2					2
2	2	6				8
3	2	6	10			18
4	2	6	10	14		32
5	2	6	10	14	18	50

### • 1.8. HUND'S RULE OF MAXIMUM MULTIPLICITY

As we pass from one element to another one of next higher atomic number, one electron is added every time to the atom. What should be the position of the incoming electron, can be predicted in accordance with Pauli's exclusion principle. On the basis of magnetic measurements, which also help to determine the electronic configuration of elements, Hund gave an empirical rule known as *Hund's rule of maximum multiplicity*. According to it,

*'Electrons are distributed among the orbitals of a sub-shell in such a way as to give the maximum number of unpaired electrons and have the same direction of spin.'*

Thus, the orbitals available at a sub-shell are first filled single before they begin to pair. In other words, pairing must begin with the entry of second electron in the *s*-orbital, fourth electron in the *p*-orbital, sixth electron in the *d*-orbital, and eighth electron in the *f*-orbital.

**Problem 1 :** Calculate the wavelength of a body of mass 1 mg moving with a velocity of  $10 \text{ ms}^{-1}$ . ( $h = 6.625 \times 10^{-34} \text{ Js}$ ).

**Solution :** We know that

$$\lambda = \frac{h}{mu}$$

Here  $m = 1 \text{ mg} = 10^{-6} \text{ kg}$ .

$$\begin{aligned} \therefore \lambda &= \frac{6.625 \times 10^{-34}}{10^{-6} \times 10} \\ &= 6.625 \times 10^{-29} \text{ m} \\ &= 6.625 \times 10^{-27} \text{ cm.} \end{aligned}$$

**Problem 2 :** Calculate the uncertainty of velocity of an electron if the uncertainty of its position is  $10^{-10} \text{ meter}$ . ( $h = 6.6 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}$  and  $m = 9.1 \times 10^{-31} \text{ kg}$ ).

**Solution :** According to Heisenberg's uncertainty principle,

$$(\Delta x)(\Delta u)(m) = \frac{h}{4\pi}$$

$$\text{or } \Delta u = \frac{h}{4\pi(\Delta x)(m)} = \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{(4)(3.14)(10^{-10} \text{ m})(9.1 \times 10^{-31} \text{ kg})}$$

$$= 5.7 \times 10^5 \text{ ms}^{-1}$$

## • 1.9. ATOMIC RADIUS

In the ordinary sense, atomic radius may be defined as the distance between the centre of the nucleus and the electron cloud of the outermost shell. It is impossible to isolate an individual atom and determine its radius because its radius is affected by the association with other atoms. Thus, a number of radii have been defined for an atom depending upon the different types of bonding between the atoms. These are :

(i) **Covalent radius :** It is defined as *one-half of the distance between the nuclei of two like atoms joined by a single covalent bond.*

For example, we know from spectroscopic data that the distance between the nuclei of two chlorine atoms in a chlorine molecule is 1.98Å. The covalent radius of chlorine atom is, therefore,  $1/2 \times 1.98 = 0.99\text{Å}$ .

(ii) **van der Waals' radius (Collision radius) :** It may be defined as *one-half of the distance between the nuclei of two nearest atoms of two adjacent molecules of an element in the solid state.* Thus, it is the distance at which the two atoms are in contact without bond formation.

For example, the distance between the nuclei of two chlorine atoms of two neighbouring chlorine molecules is 3.60Å, the van der Waals' radius of chlorine is, therefore,  $1/2 \times 3.60 = 1.80\text{Å}$ .

(iii) **Crystal radius (Metallic or atomic radius) :** *It is defined as one-half of the distance between the nuclei of two adjacent metal atoms in the metallic close packed crystal lattice.*

For example, the internuclear distance between two adjacent sodium atoms in a crystal of the metal is 3.72Å. The crystal radius of sodium is, therefore,  $1/2 \times 3.72 = 1.86\text{Å}$ . The crystal radii are about 10-15% higher than the single bond covalent radii.

(a) **Variation of atomic radius with atomic number :** In general, atomic radius depends upon the number of shells and nuclear charge.

(b) **Variation of atomic radius in a group :** *In general, atomic radius increases in a group as the atomic number increases.*

The number of shells increases in a group and, therefore, the atomic radius increases. For example, the covalent radii of the elements of IA group are given below :

$$\text{Li} = 1.34\text{Å}, \text{Na} = 1.57\text{Å}, \text{K} = 1.96\text{Å}, \text{Rb} = 2.11\text{Å}, \text{Cs} = 2.25\text{Å}.$$

(c) **Variation of atomic radius in a period :** *In a period the atomic radius decreases as the atomic number increases.* There should be no effect on atomic radius due to this factor. On the other hand, there is an increase in the nuclear charge. Therefore, the shells are attracted more and more strongly towards the nucleus. Thus, the atomic radius decreases in a period as the atomic number increases. For example, the covalent radii of the elements of the second period are given as :

Element	${}_3\text{Li}$	${}_4\text{Be}$	${}_5\text{B}$	${}_6\text{C}$	${}_7\text{N}$	${}_8\text{O}$	${}_9\text{F}$	${}_{10}\text{Ne}$
Electronic configuration	(2, 1)	(2, 2)	(2, 3)	(2, 4)	(2, 5)	(2, 6)	(2, 7)	(2, 8)
Covalent radii	1.34Å	0.90Å	0.82Å	0.77Å	0.75Å	0.73Å	0.72Å	—

## • 1.10. IONIC RADIUS

Ionic radius is defined as *the distance between the centre of the nucleus of an ion and the point upto which the nucleus has influence on its electron cloud.* The limit of electron cloud around nucleus cannot be determined with certainty. Therefore, the radius of an ion is determined by determining the internuclear distance in an ionic compound by X-ray measurements. This distance is then taken as the sum of the radii of the two ions involved. If we know the radius of one ion, we can calculate the radius of the other.

The atoms change into ions either by the loss or gain of electrons. A cation is always smaller than the corresponding atom, whereas anion is always bigger than the corresponding atom.

(a) **Variation of ionic radii in a group** : Since the atomic size increases as we move down the group, therefore, ionic radius also increases in moving from top to bottom in a group. For example, ionic radius of alkali metals may be represented as :

Alkali metal ion	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
Ionic radii	0.68Å	0.95Å	1.33Å	1.48Å	1.69Å

(b) **Variation of ionic radii in a period** : Since the atomic size decreases in a period, therefore, ionic radius also decreases. In a period, the ionic radii of cations of elements of groups I-III and also anions of the elements of groups V-VII decrease with the increase in atomic number.

Groups	I	II	III	V	VI	VII
Cations	Na <sup>+</sup>	Mg <sup>2+</sup>	Al <sup>3+</sup>	N <sup>3-</sup>	O <sup>2-</sup>	F <sup>-</sup>
Ionic radii	0.95Å	0.65Å	0.50Å	1.71Å	1.40Å	1.36Å

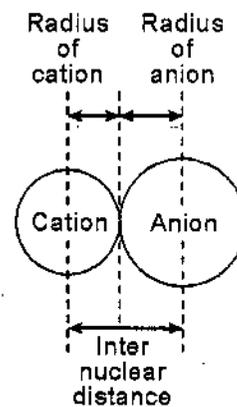


Fig. 3

### • 1.11. IONIZATION ENERGY (IONIZATION POTENTIAL)

The minimum energy required to remove most loosely bound electron from the isolated gaseous atom is known as ionization potential or ionization energy. The most loosely bound electron means the electron present in the outermost shell.

This energy is generally measured in electron volt per atom (e.v./atom) or kilo calories per mole (k. cal/mole) or kilo joule per mole (kg/mole). The electrons are removed in stages one by one. Consequently, there may be first, second, third or *n*th ionization potential, depending upon the removal of first, second, third or *n*th electron from the atom.

(a) **Variation of ionization potential in a group** : In general, the ionization potential decreases in a group as the atomic number increases. This is because in a group, atomic size increases. On account of this, the outer electrons are attracted less and less strongly by the nucleus. For example, the first ionization potential of alkali metals are :

$$\text{Li} = 5.4 \text{ e.v.}; \quad \text{Na} = 5.1 \text{ e.v.}; \quad \text{K} = 4.3 \text{ e.v.}; \quad \text{Rb} = 4.2 \text{ e.v.}; \quad \text{Cs} = 3.9 \text{ e.v.}$$

(b) **Variation of ionization potential in a period** : In general, the ionization potential increases in a period as the atomic number increases. This is, because in a period the nuclear charge increases and the atomic size decreases. On account of this, the electrons are attracted more and more strongly by the nucleus.

#### (c) Applications in explaining the chemical behaviour

(i) The elements having lower value of ionization potential e.g. alkali and alkaline earth metals are more reactive, strong reducing agents and are basic in nature.

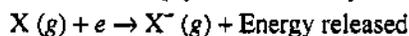
(ii) The elements having higher value of ionization potential are less reactive, strong oxidizing agents and are acidic in nature (except inert elements).

(iii) The relative value of ionization potential and electron affinity of two elements gives an idea about the nature of bond formed between two elements. If the difference between both the values is greater, the bond will be more ionic and if the difference is less, the bond will be more covalent.

(iv) The value of ionization potential gives an evidence about the number of valency electrons in the atom. For example, in the case of sodium, the second ionization potential (47.3 e.v.) is too much higher than the first ionization potential (5.1 e.v.). This indicates the presence of one electron in valency shell of sodium.

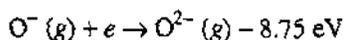
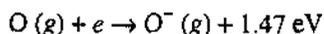
### • 1.12. ELECTRON AFFINITY

The chemical properties of the elements are also determined by the tendency of their atoms to accept an additional electron. This tendency is measured by the electron affinity, i.e., the energy released when a gaseous atom accepts an electron forming a free gaseous ion.



The energy released is measured in electron volt per atom (e.v./atom) or kilo joule per mole (k.j./mole). Thus, larger is the energy released, the greater is the electron affinity. In other words, it is a measure of the force with which the added electron is bound by the nucleus of the atom.

There may be first, second or higher electron affinities just like ionization potential



The second and higher order electron affinities are always negative because there occurs a repulsion between negatively charged ion and electron being added and energy has to be given for this addition of electron.

The electron affinities of some of the elements have been determined by absorption spectroscopy and are given in the following table :

							He
							0
Li	Be	B	C	N	O	F	Ne
0.58	0	0.33	1.13	0.20	1.47	3.62	0
Na	Mg	Al	Si	P	S	Cl	Ar
0.78	0	0.52	1.39	0.80	2.07	3.82	0
						Br	Kr
						3.54	0
						I	Xe
						3.24	0

(a) **Variation of electron affinity in a group :** *In general, the electron affinity decreases in a group as the atomic number increases.* This is because the atomic size increases and, therefore, effective nuclear attraction for the electron decreases.

It is observed from the above table, that the elements of the second period, *i.e.*, from lithium to fluorine, have lower electron affinity than the next lower members in their respective groups. This abnormal behaviour is due to the fact that in these elements, the added electron will go to the second shell which is comparatively small. Thus, there is a large repulsion between the electrons already present and the electron being added to the atom. In such cases, a small amount of energy released is utilized in overcoming these forces of repulsion.

(b) **Variation of electron affinity in a period :** *In general, electron affinity increases in a period as the atomic number increases.* In a period, the nuclear charge increases and the atomic size decreases. Therefore, the tendency of the atom to attract additional electron increases and hence electron affinity increases in a period.

(c) **Application in explaining the chemical behaviour :**

(i) The elements having higher value of electron affinity can easily accept additional electron. These elements are electronegative. They can easily form anions and ionic compounds.

(ii) The elements having higher value of electron affinity act as strong oxidizing agents, *e.g.*, halogens.

(iii) The relative values of ionization potential and electron affinity give an idea about the nature of bond formed between two elements.

### • 1.13. ELECTRONEGATIVITY

*The tendency of an atom in a compound to attract shared electrons towards itself is known as electronegativity of the atom.*

Pauling gave an arbitrary scale to measure the electronegativity of different elements. This scale is based upon the calculation of bond energies. In this scale, fluorine has the maximum value of electronegativity, *i.e.*, 4.0, whereas noble gases have the minimum value, *i.e.*, 0.0.

On Mulliken scale, the average of ionization potential and electron affinity is known as electronegativity. In general, the smaller atoms as well as the atoms with nearly filled shells of electrons, attract electrons more than larger atoms and are, therefore, more electronegative.

(a) **Variation of electronegativity in a group :** *In general, the electronegativity decreases in a group as the atomic number increases.* This is because in a group the atomic size increases, consequently the added electron is at a larger distance from the nucleus and is, therefore, held less tightly. For example, the electronegativity values on the Pauling scale of the alkali metals are given below :

Alkali metal	Li	Na	K	Rb	Cs	Fr
Electronegativity	1.0	0.9	0.8	0.8	0.7	0.7

(b) **Variation of electronegativity in a period.** In general, the electronegativity increases in a period with the increase of atomic number. This is because in a period, the nuclear charge increases and the atomic size decreases. The atom, therefore, attracts the electrons more strongly. For example, the electronegativity values of the elements of the second period are given below :

2nd Period	Li	Be	B	C	N	O	F
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0

(c) **Applications in explaining the chemical behaviour :**

(i) **Metallic and non-metallic character of elements :** The element having lesser value of electronegativity will be a metal whereas an element having higher value of electronegativity will be a non-metal.

(ii) **Diagonal relationship :** The diagonally placed elements of second and third period of the periodic table show many similar properties due to almost same electronegativity of the elements.

(iii) **Nature of bond :** With the help of electronegativity values, it is possible to predict the nature of the bond formed between two atoms. If there is a large difference between the electronegativities of the two atoms, the bond formed will be ionic or polar in character. On the other hand, if the difference is small, the bond formed will be covalent or non-polar in character.

Pauling gave a rule by which the nature of the bond formed between two atoms can be predicted. According to this rule, *if the electronegativity difference between two atoms is 1.7, the bond is 50% ionic in character and when the difference is more than 1.7, the bond is correspondingly more ionic.*

(iv) **Stability of bond :** The greater is the difference in the electronegativity of two atoms, more stable will be the bond.

HX Molecule	H—F	H—Cl	H—Br	H—I
Electronegativity difference	1.9	0.9	0.7	0.4

Stability of H—X bond decreases  $\rightarrow$

(v) **Bond length :** Schomaker and Stevenson (1941) gave the following relation to calculate the covalent radius :

$$d_{A-B} = r_A + r_B - 0.09(x_A - x_B)$$

where  $r_A$  and  $r_B$  are the covalent radii of the atoms A and B and  $x_A$  and  $x_B$  are their electronegativities.

(vi) **Acid Base character of the oxides of the elements of the same period :** The electronegativity difference between an element and oxygen predicts the nature of oxide formed by the element. If the difference of electronegativity between the two is large, the oxide is basic and if the said difference is small, the oxide will be acidic.



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**• SUMMARY**


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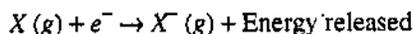
- According to de Broglie, the wavelength ( $\lambda$ ) of a particle of mass  $m$  and velocity  $u$  is given by the relation  $\lambda = \frac{h}{mu}$ .

- **Heisenberg's uncertainty principle** : It is impossible to determine simultaneously both the position and the velocity or momentum of a small moving particle like an electron.

- The Schrodinger's wave equation is given by,

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

- According to **aufbau's principle**, the electrons are first accommodated in the orbitals of lowest energy, viz.,  $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d$  etc.
- According to **Pauli's exclusion principle**, no two electrons in a given atom can have the same four quantum numbers.
- **Hund's rule** : Electrons are distributed among the orbitals of a sub-shell in such a way as to give the maximum number of unpaired electrons and have the same direction of spin.
- **Covalent radius** : It is one half of the distance between the nuclei of two like atoms joined by a single covalent bond.
- **Ionic radius** : It is the distance between the centre of the nucleus of an ion and the point upto which the nucleus has influence on its electron cloud.
- **Ionization energy** : It is the minimum energy required to remove most loosely bound electron from the isolated gaseous atom. It is expressed in  $\text{kJ mole}^{-1}$ .
- **Electron affinity** : It is the energy released when a gaseous atom accepts an electron forming a free gaseous ion.



- **Electronegativity** : It is the tendency of an atom in a compound to attract shared electrons towards itself.
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**• TEST YOURSELF**


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Answer the following questions :

1. Explain the dual nature of an electron.
2. Write de Broglie's equation.
3. Define Heisenberg's uncertainty principle. Describe the relation between uncertainty and probability.
4. Mention Schrodinger's wave equation.
5. Define quantum numbers and explain their significance in characterising an electron in an atom.
6. Explain aufbau principle.
7. State and explain Pauli's exclusion principle.
8. Explain Hund's rule of maximum multiplicity.
9. A body moving with a speed of  $100 \text{ ms}^{-1}$  has a de Broglie wavelength  $5 \times 10^{-10} \text{ m}$ . Calculate the mass of the body, where  $h = 6.625 \times 10^{-34} \text{ Js}$ .
10. Explain atomic radius. How it changes within a group and a period of the periodic table?
11. Define ionic radius. Why is cation smaller and anion larger than its atom?
12. State and explain ionization energy. Describe its applications in explaining the chemical behaviour.
13. Define and explain electron affinity. How does it change in a group and in a period of periodic table?
14. State and explain electronegativity. How does it vary in a group and in a period of the periodic table?
15. Describe the applications of electronegativity in explaining the chemical behaviour.
16. Which of the following has the maximum electronegativity?  
(a) C                      (b) O                      (c) N                      (d) B
17. Which has the maximum ionic radius?  
(a) Ne                      (b) F                      (c) O                      (d) N
18. The magnetic quantum number is related to :  
(a) Shape                      (b) Size                      (c) Orientation                      (d) Spin

**19. Fill in the blanks :**

- (i) The element with maximum electronegativity in the periodic table is .....
- (ii) A cation is ..... than the parent atom, while an anion is ..... than the parent atom.
- (iii) Atomic radius of fluorine is ..... than that of neon.

**ANSWERS**

9.  $1.325 \times 10^{-26}$  kg 16. (b) 17. (a) 18. (c) 19. (i) fluorine (ii) smaller, bigger (iii) less



## 2

## CHEMICAL BONDING

## STRUCTURE

- Valency Bond Theory
- Hybridization
- Ionic Structures
- Fajan's Rule
- Inert Pair Effect
- Odd Electron Bond
- Singlet Bond
- Hydrogen Bond
- Student Activity
- Summary
- Test Yourself

## LEARNING OBJECTIVES

After going this unit you will learn :

- $sp^3$ ,  $sp^2$  and  $sp$ -hybridization and shapes of covalent molecules.
- Radius ratio rule and its limitations.
- Sodium chloride structure and shapes of ionic crystals.
- Characteristics of one electron bond and three electron bond.
- Structure of  $PCl_5$  and  $SF_6$ .
- Intermolecular and intramolecular hydrogen bonding and the nature of hydrogen bond.

## 2.1. VALENCY BOND THEORY

According to Lewis concept, a covalent bond is formed by the mutual sharing of electrons between the two atoms. This concept could not explain the nature of forces which hold the two atoms together in a covalent molecule. In order to explain the nature of these forces, Heitler and London in 1927 put forward valency bond theory which was later on extended by Pauling and Slater in 1931. This theory is based upon the pairing and resultant neutralization of opposed electron spins. Heitler and London calculated the energy of two interacting hydrogen atoms when they are brought from large distances to form a hydrogen molecule. The energy curves so obtained may be represented in fig. (i).

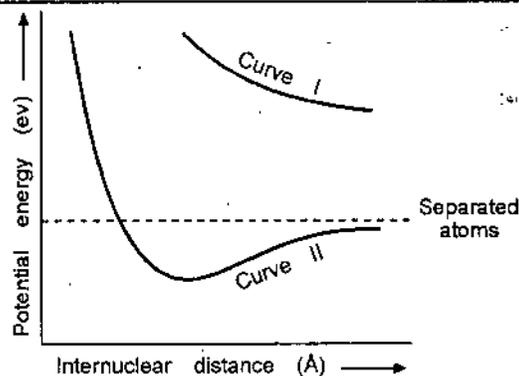


Fig. 1.

The spins of the electrons of two hydrogen atoms may be in the same direction, *i.e.*,  $H(\uparrow)$  and  $H(\uparrow)$  or in the opposite directions,  $H(\uparrow)$  and  $H(\downarrow)$ . When two hydrogen atoms having similar spins of their electrons are brought nearer to one another, the potential energy of the system increases as shown by curve I. This is due to the strong repulsive forces between the electrons of similar spins. When two hydrogen atoms having opposite spins of their electrons are brought nearer to one another, the potential energy of the system decreases as shown by curve II. As the distance between the two atoms decreases, there occurs an increase in the force of attraction and ultimately a critical internuclear distance is reached at which the potential energy of the system is minimum. On further decreasing the internuclear distance, the potential energy of the system again increases. This is

because at such short distances, the forces of repulsion between the two nuclei predominate and the molecule becomes unstable. The dissociation energy of  $H_2$  molecule is 103.2 k. cal/mole, *i.e.*, it is the energy required to dissociate  $H_2$  molecule into atoms. Thus, it is evident that the same amount of energy will be released when the bond is formed between two hydrogen atoms. The minima in curve II shows bond formation.

At critical internuclear distance, the electron of one atom moves to the other atom and vice versa, *i.e.*, an exchange of electron may take place. Each electron has an equal possibility of being found on either atom and each nucleus may be associated with both electrons. Thus, it is not possible to distinguish the two electrons after the bond formation, *i.e.*, it cannot be said as to which electron belongs to which atom. Due to exchange of electrons, the exchange forces develop which further stabilize the molecule.

The formation of a stable bond between two atoms having electrons of opposite spins is also in accordance with the Pauli's exclusion principle. Each electron possesses a magnetic dipole because of its spin. When the spins of two electrons are opposite in an orbital, the mutual neutralization of dipole moments results in an attractive force which is responsible for holding the atoms together in a molecule. According to orbital concept, a covalent bond is formed by the overlapping of atomic orbitals. As a result, there is an increase in the electron density wherever the overlapping occurs, *i.e.*, at the mid point between the two atoms. Thus, the electrostatic attraction between the nuclei and accumulated electron cloud is responsible for holding the atoms together in a molecule.

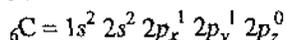
The theory can be extended to other molecules if their atoms have unpaired electrons. If the electrons are not unpaired in the ground state, there must be present vacant orbitals of slightly higher energy of the same main energy level to accommodate the previously paired electrons in the separate orbitals. The energy needed to unpair the electrons is utilized from the energy released when a covalent bond is formed. Thus, nitrogen with outer configuration  $2s^2 2p_x^1 2p_y^1 2p_z^1$  can form only three bonds as in  $NCl_3$ . Nitrogen cannot form  $NCl_5$  as it does not have vacant *d*-orbitals to accommodate one of the unpaired *s* electrons. On the other hand, phosphorus with an outer configuration  $3s^2 3p_x^1 3p_y^1 3p_z^1$  can also form  $PCl_5$  as phosphorus atom has vacant *d*-orbitals to accommodate one of the unpaired *s* electrons.

**Limitations of valency bond theory :** This theory does not explain :

- (i) The formation of coordinate bond in which shared pair of electrons is contributed by only one of the combining atoms.
- (ii) The paramagnetic nature of oxygen molecule.
- (iii) The structures of odd electron molecules or ions where no pairing of electrons take place.
- (iv) The directional nature of covalent bond.
- (v) The formation and structures of several compounds involving resonance and hybridization.

## • 2.2. HYBRIDIZATION

The formation of compounds of beryllium, boron, carbon and many other elements could not be explained simply by the concept of overlapping of atomic orbitals. For example, the electronic configuration of carbon is :



In the ground state, carbon has two unpaired electrons. Therefore, it should be divalent but it is found to be tetravalent in almost all its compounds. The tetravalency of carbon may be explained

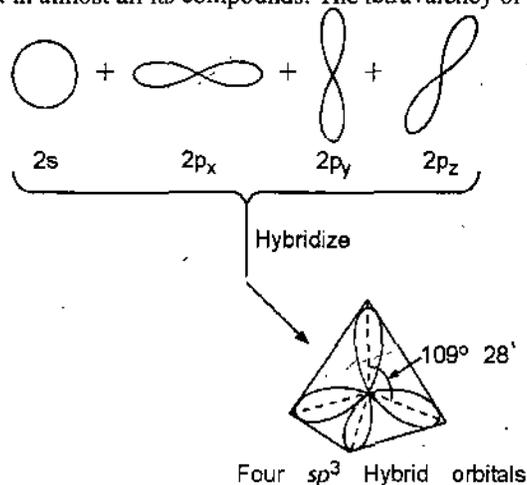


Fig. 2.  $sp^3$ -hybridization

by assuming that one of two  $2s$  electrons is excited to vacant  $2p_z$  orbitals, thus giving the configuration as  $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$ . Now the carbon atom has four unpaired electrons and, therefore, it can form four bonds, three of which formed by three  $p$ -orbitals will be at right angles to one another and fourth formed by  $s$ -orbital will have no directional preference. Accordingly, the three bonds should be of one type and fourth should be of another. But in actual practice, all the four bonds of carbon are equivalent in all respects. To explain this, it is assumed that four atomic orbitals of carbon ( $2s$ ,  $2p_x$ ,  $2p_y$  and  $2p_z$ ) get mixed up and form four equivalent hybrids of equal energy.

The phenomenon of mixing up of atomic orbitals of similar energies and formation of equivalent number of entirely new orbitals of identical shape and energy is known as hybridization. The new orbitals so formed are called hybrid orbitals. The bonds formed by these orbitals are stronger than the bonds formed by pure  $s$ ,  $p$  or  $d$ -orbitals.

The four new bonds, thus formed are directed towards the four corners of regular tetrahedron and are inclined to each other at an angle of  $109^\circ 28'$ . The whole phenomenon may be represented as shown in fig. (2).

Since in the above case, the hybridization has taken place by the combination of one  $s$  and three  $p$ -orbitals, it is called as  $sp^3$  hybridization.

### Type of hybridization and shapes of covalent molecules

(i)  **$sp$ -Hybridization** : The combination of one  $s$  and one  $p$ -orbitals to form two hybrid orbitals of equal energy is known as  $sp$  hybridization. This type of hybridization [Fig. 3] is found in beryllium compounds like  $\text{BeF}_2$ ,  $\text{BeCl}_2$  etc.

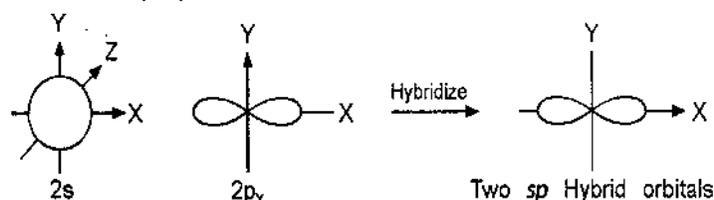
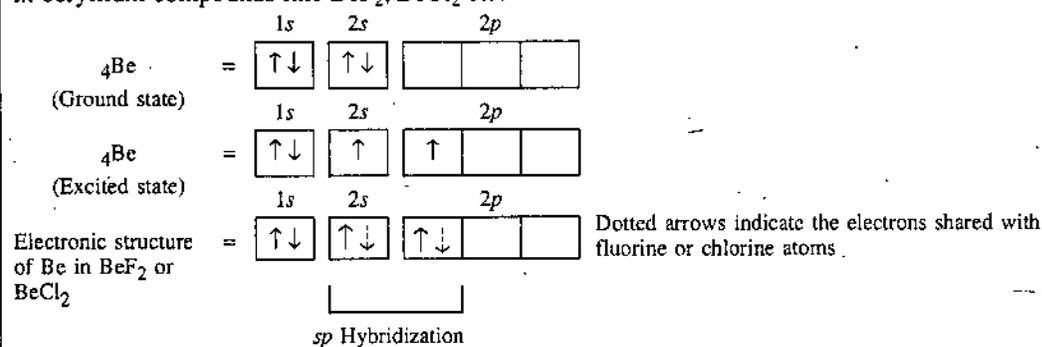
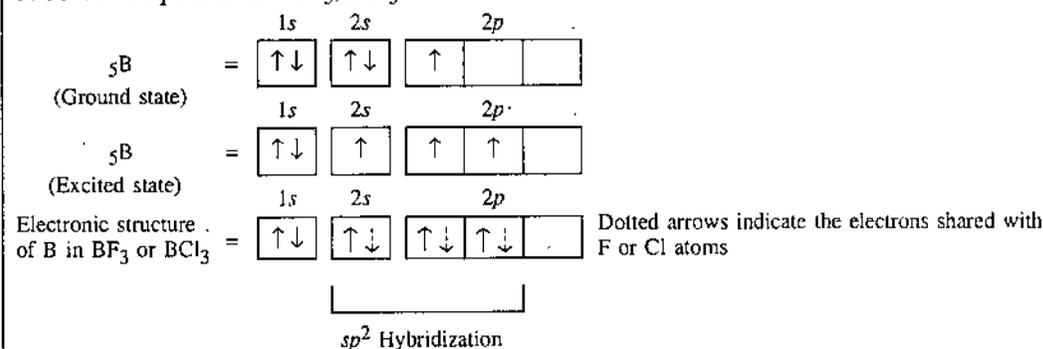


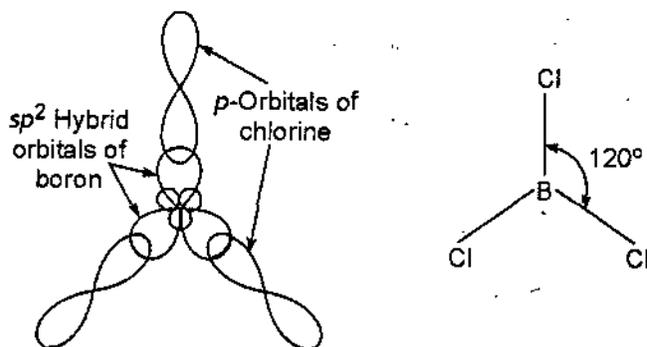
Fig. 3. Structure of  $\text{BeF}_2$  molecule

The molecules involving this type of hybridization are linear with a bond angle of  $180^\circ$ . Other common examples of  $sp$ -hybridization are  $\text{CO}_2$ ,  $\text{HgCl}_2$ ,  $\text{C}_2\text{H}_2$  etc.

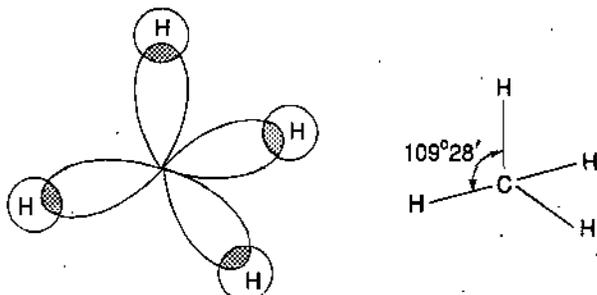
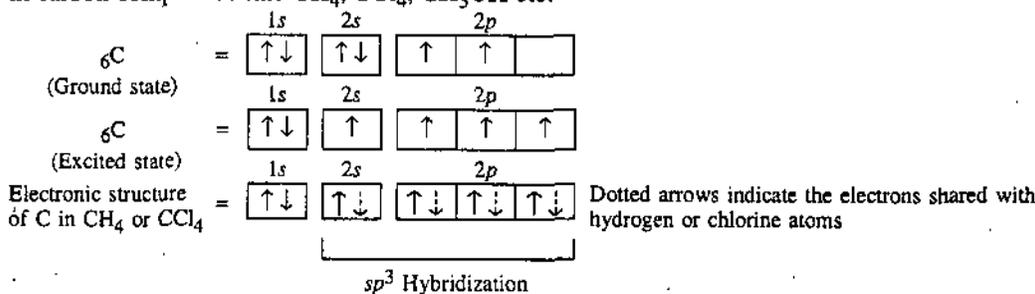
(ii)  **$sp^2$ -Hybridization** : The combination of one  $s$  and two  $p$ -orbitals to form three hybrid orbitals of equal energy is known as  $sp^2$ -hybridization. This type of hybridization [Fig. 4] is found in boron compounds like  $\text{BF}_3$ ,  $\text{BCl}_3$  etc.



The molecules involving this type of hybridization are plane triangular with a bond angle of  $120^\circ$ . Other common examples of  $sp^2$  hybridization are  $\text{SO}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ , benzene etc.

Fig. 4. Structure of  $\text{BCl}_3$  molecule.

(iii)  $sp^3$ -Hybridization : The combination of one  $s$  and three  $p$ - orbitals to form four hybrid orbitals of equal energy is known as  $sp^3$ -hybridization. This type of hybridization [Fig 5] is found in carbon compounds like  $\text{CH}_4$ ,  $\text{CCl}_4$ ,  $\text{CH}_3\text{OH}$  etc.

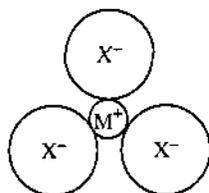
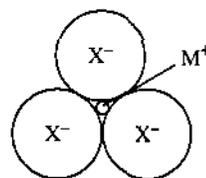
Fig. 5. Structure of  $\text{CH}_4$  molecule.

### • 2.3. IONIC STRUCTURES

[I] **Coordination Number** : The ionic compound is a cluster of ions in which positive ions are surrounded by greater possible number of negative ions and vice versa. *The number of oppositely charged ions surrounding any particular ion in the crystal is known as coordination number of that ion.* For example, in the crystal lattice of  $\text{NaCl}$ , each  $\text{Na}^+$  ion is surrounded by six  $\text{Cl}^-$  ions and each  $\text{Cl}^-$  ion is surrounded by six  $\text{Na}^+$  ions. Thus, in this case, the coordination number of both  $\text{Na}^+$  and  $\text{Cl}^-$  ions is six. Similarly, in the crystal lattice of  $\text{CaF}_2$ , each  $\text{Ca}^{2+}$  ion is surrounded by eight  $\text{F}^-$  ions but each  $\text{F}^-$  ion is surrounded by four  $\text{Ca}^{2+}$  ions. Thus, the coordination number of  $\text{Ca}^{2+}$  ions is eight whereas that of  $\text{F}^-$  ions is four.

[II] **Radius Ratio Rule and Shapes of Ionic Crystals** : The coordination number and shape of an ionic crystal depend upon the ratio of the cationic and anionic radius. *The effect of radius ratio in determining the coordination number and shape of an ionic crystal is known as radius ratio rule.*

Whatever be the arrangement of ions in the crystal, a limiting case of radius ratio arises when the ions are in contact with one another. For example, when the coordination number of an ion  $\text{M}^+$  is three in an ionic compound  $\text{MX}$ , the three  $\text{X}^-$  ions will be in contact with one  $\text{M}^+$  ion in the following two ways :

Fig. 6 (a) When  $X^-$  ions are apart.Fig. 6 (b) When  $X^-$  ions are in contact with each other

Thus, if we know the radii of the cation and anion of an ionic crystal, it is easy to calculate the radius ratio and with the help of the table given below, we can know the coordination number and geometric shape of the crystal.

S.N.	Limiting radius ratio $r_c^+/r_a^-$	Coordination number	Shape of the crystal	Possible example
1.	0.155 to 0.225	3	Plane triangle	Boron oxide
2.	0.225 to 0.414	4	Tetrahedral	ZnS
3.	0.414 to 0.732	4	Square planar	
4.	0.414 to 0.732	6	Octahedral	NaCl
5.	0.732 to 1.000	8	Body centred cubic	CsCl

**Ionic Compounds of AX Type :** The ionic compounds of AX type include the structures of NaCl, CsCl and ZnS.

(i) **Sodium chloride structure :** In NaCl, the radius ratio  $\frac{0.95}{1.81}$  has been found to be 0.524,

which suggests it to be either octahedral or square planar in shape. The X-ray study of the crystal shows that it has an octahedral structure. Each  $Na^+$  ion is surrounded by six  $Cl^-$  ions and vice versa. Hence, the coordination number of both  $Na^+$  and  $Cl^-$  ions is six. In this structure, the  $Cl^-$  ions are arranged in face centred cubic type of symmetry. The structure of NaCl may be represented as :

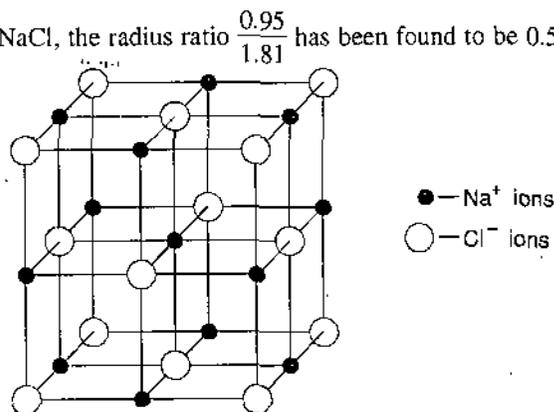


Fig. 7. Structure of NaCl

The compounds like NaI, KCl and MgO, have similar type of structures.

### [III] Limitations of Radius Ratio Rule :

(i) The radius ratio rule is applicable for the packing of rigid spheres. The larger anions are easily polarized by the cations and bonding has some covalent character. Covalent bonds are directional. Hence, radius ratio rule is not strictly applicable to ionic solids which have partial covalent character. For example, in AgI the radius ratio  $\frac{r_{Ag^+}}{r_I^-}$  is found to be 0.52 which indicates the coordination number 6 but its coordination number is 4 and it is tetrahedral. Similarly, in  $ZnO$ , the radius ratio,  $\frac{r_{Zn^{2+}}}{r_{O^{2-}}}$  is 0.528 but has tetrahedral structure.

(ii) There are some compounds which occur in more than one form with different coordination numbers. In such cases, anion-anion repulsions and internuclear distances will be different. For example, TiCl crystallizes out as NaCl structure (coordination number 6) with internuclear distance 3.15 Å as well as CsCl structure (coordination number 8) with internuclear distance 3.32 Å.

## • 2.4. FAJAN'S RULES

Fajan in 1924 gave certain rules with the help of which it is possible to know the conditions under which electrovalency passes into covalency. When two oppositely charged ions approach each other closely, the cation attracts the electron atmosphere of the anion (electrostatic attraction) and simultaneously repels the anion nucleus. This results in the deformation, distortion or polarization of the anion. Similarly, the anion also polarizes the cation but the effect will be negligible

or less pronounced because of smaller size of cation. The net result of this ion polarization is that there occurs some sharing of electrons between the two ions, *i.e.*, the bond becomes partly covalent in character.

The polarization or deformation of ions depends upon a number of factors known as Fajan's rules.

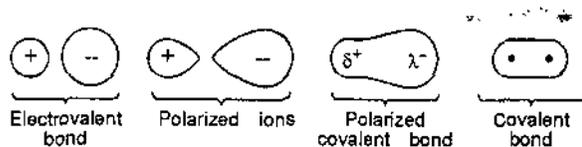


Fig. 8. Transition between ionic and covalent bonding.

(i) **Large charge on the ions :** The greater the charge on cation or anion or both, greater will be the forces of attraction between the oppositely charged ions and, thus, there will be more chances of electrovalency to pass into covalency. For example,  $\text{Al}^{3+}$  ion (cationic charge + 3) will distort the chloride ions more than  $\text{Na}^+$  ion (cationic charge + 1). Thus,  $\text{AlCl}_3$  is covalent whereas  $\text{NaCl}$  is ionic.

(ii) **Small size of the cation :** A small cation polarizes the anion more than a large cation. This is because of its greater attractive force for the electron of the anions. For example, in the IIA group, the  $\text{Be}^{2+}$  ion has the least size and has the greatest polarizing effect. Thus,  $\text{BeCl}_2$  is the most covalent among the chlorides of IIA group elements.

(iii) **Large size of the anion :** A large anion is more easily polarized by the cation than a small anion. This is because the outer electrons of the large anion are less strongly held by its nucleus and, therefore, more strongly attracted by the cation. For example,  $\text{AlCl}_3$  is covalent whereas  $\text{AlF}_3$  is ionic.

(iv) **A cation with non-noble gas configuration :** The cations having non-noble gas type of electronic configuration ( $s^2 p^6 d^{1-10}$ ) of their outermost shells polarize the anions more strongly than the cations having noble gas type of electronic configuration ( $s^2 p^6$ ). This is because the d-electrons in such cations screen the nuclear charge less effectively than s and p electrons of cations having noble gas type of electronic configurations. As a result, the cations having non-noble gas type of electronic configurations behave as if they had greater charge. For example, the halides of copper (I) and silver (I) are more covalent than the corresponding halides of sodium and potassium although the charge on the ions is the same (+1) and their ionic sizes are similar.

(v) **Nature of the solvent :** The solvents having high dielectric constant, *e.g.*, water weakens the electrostatic forces between the ions and, thus, decrease the tendency of electrovalency to pass into covalency.

### Some Examples Illustrating Fajan's Rule

(a)  **$\text{CuO}$  or  $\text{CuS}$  :**  $\text{CuS}$  will be more covalent than  $\text{CuO}$ . This is because in these compounds, cation ( $\text{Cu}^{2+}$ ) is the same, but  $\text{S}^{2-}$  ion is bigger in size than  $\text{O}^{2-}$  ion. Thus,  $\text{Cu}^{2+}$  ion will polarize  $\text{S}^{2-}$  ion more than  $\text{O}^{2-}$  ion.

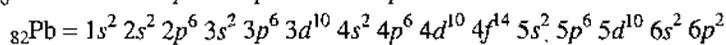
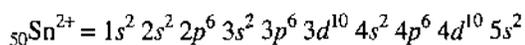
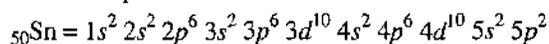
(b)  **$\text{LiCl}$  or  $\text{NaCl}$  :**  $\text{LiCl}$  will be more covalent than  $\text{NaCl}$ . This is because in these compounds, anion ( $\text{Cl}^-$ ) is the same, but  $\text{Li}^+$  ion has smaller size than  $\text{Na}^+$  ion. Thus,  $\text{Li}^+$  ion will polarize  $\text{Cl}^-$  ion more than  $\text{Na}^+$  ion.

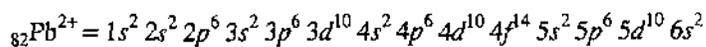
(c)  **$\text{AlCl}_3$  or  $\text{AlF}_3$  :**  $\text{AlCl}_3$  will be more covalent than  $\text{AlF}_3$ . In these compounds, the cation ( $\text{Al}^{3+}$ ) is the same but  $\text{Cl}^-$  ion is bigger than  $\text{F}^-$  ion. Thus  $\text{Al}^{3+}$  ion will polarize  $\text{Cl}^-$  ions, the  $\text{F}^-$  ion is very small and cannot be polarized by  $\text{Al}^{3+}$  ion.

(d)  **$\text{SnCl}_2$  or  $\text{SnCl}_4$  :**  $\text{SnCl}_4$  will be more covalent than  $\text{SnCl}_2$ . This is because in  $\text{SnCl}_4$ , the  $\text{Sn}^{4+}$  ion has greater charge than  $\text{Sn}^{2+}$  ion in  $\text{SnCl}_2$ . As a result,  $\text{Sn}^{4+}$  ion will polarize the  $\text{Cl}^-$  ions more strongly than  $\text{Sn}^{2+}$  ion.

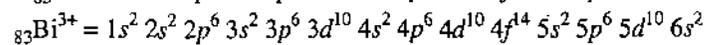
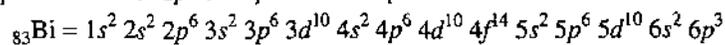
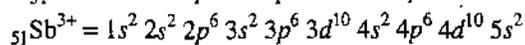
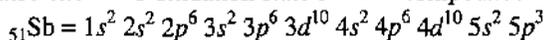
## 2.5. INERT PAIR EFFECT

Some of the heavier p-block elements, in addition to their group number oxidation state, also show lower oxidation states equal to their group number minus two. For example, the heavier elements of the IV A group, *i.e.*, Sn and Pb in addition to + 4 oxidation state, also show + 2 oxidation state in their compounds.





Similarly, the heavier elements of the V A group, i.e., Sb and Bi in addition to + 5 oxidation state, also show + 3 oxidation state in their compounds.



Thus, it is clear that the lower oxidation states arise when the *s*-electrons of the outermost shell do not take part in the bond formation and become inert.

*The reluctance of the s-electron pair to take part in the bond formation is known as inert pair effect.*

This effect is more marked in the heavier elements. Thus, the pair of *s*-electrons is more inert in lead than in tin. Therefore,  $\text{Pb}^{2+}$  ion is more stable than  $\text{Sn}^{2+}$  ion. Similarly,  $\text{Bi}^{3+}$  ion is more stable than  $\text{Sb}^{3+}$  ion.

The explanation of inert pair effect is that the outer  $ns^2$  electrons penetrate to some extent to the penultimate shell. As a result, the  $ns^2$  electrons are less effectively screened from the nucleus and hence are strongly held by the atom.

## • 2.6. ODD ELECTRON BOND

The bonds in which odd number of electrons are involved in bond formation are known as odd electron bonds. When there is a sharing of one, three or sometimes five electrons between two atoms, the bond formed is known as one electron bond, three electron bond or five electron bond, respectively. The molecules having odd electron bonds are very reactive.

### [I] One Electron Bond

One electron type of bond is formed between two hydrogen atoms in hydrogen molecule ion ( $\text{H}_2^+$ )

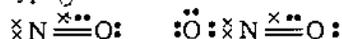


The characteristics of one electron bond are as follows :

- (i) This bond is formed only between two like atoms.
- (ii) This bond is weaker than normal covalent bond. Its dissociation energy is 54 k. cal/mole, whereas dissociation energy of hydrogen molecule is 103.2 k. cal/mole.
- (iii) One electron bond has more bond length than single covalent bond. The bond length of one electron bond is 1.06 Å whereas that of single covalent bond in  $\text{H}_2$  molecule is 0.74 Å.
- (iv) The compounds having this bond are paramagnetic.

### [II] Three Electron Bond

Three electron type of bond is found in NO and  $\text{NO}_2$  molecules.



The characteristics of three electron bond are as follows :

- (i) This bond is formed between atoms of approximately similar electronegativity.
- (ii) It's bond energy is less than two electron bond.
- (iii) It has more bond length than two electron bond.

## • 2.7. SINGLET BOND

In order to explain the formation of compounds like  $\text{PCl}_5$ ,  $\text{SF}_6$  etc., Sidgwick suggested that the octet is maintained even in such cases by means of singly shared electrons. *The way of chemical combination involving sharing of one electron between two atoms is known as singlet bond, single electron bond or half bond.* It is a special type of coordinate bond and is represented by a half arrow

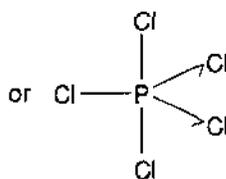
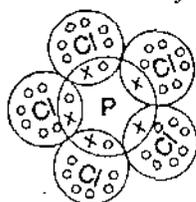


Fig. 8. Structure of  $\text{PCl}_5$

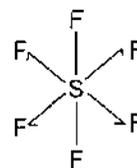
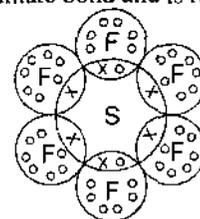
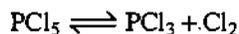


Fig. 9. Structure of  $\text{SF}_6$

head ( $\rightarrow$ ) pointing away from donor to the acceptor atom. For example, the structures of  $\text{PCl}_5$  and  $\text{SF}_6$  are shown in figures 8 and 9.

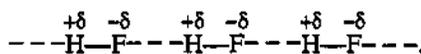
This view is also supported by the fact that  $\text{PCl}_5$ , on heating, dissociates to give  $\text{PCl}_3$  and  $\text{Cl}_2$ , thus, indicating that in  $\text{PCl}_5$ , three bonds are of one type and two are of another type.



## • 2.8. HYDROGEN BOND

In the compounds of hydrogen with strongly electronegative elements such as fluorine, oxygen and nitrogen, the shared pair of electrons is attracted more towards the electronegative atom. As a result, the electronegative atom acquires a partial negative charge and hydrogen acquires a partial

positive charge ( $\text{H}^{\delta+}-\text{F}^{\delta-}$ ). Such a molecule behaves as a dipole because one end of the molecule carries a positive charge and the other carries a negative charge. If a number of such molecules are brought together, the positive end of one molecule will attract and will be attracted by the negative end of other molecule. In this way, two or more molecules will be associated together to form large clusters of molecules.

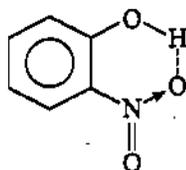
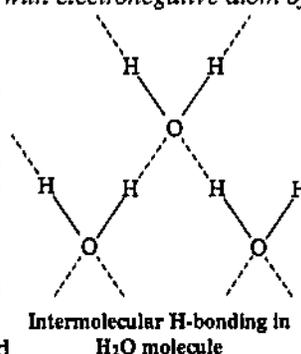


The attractive force, that binds hydrogen atom of one molecule with electronegative atom of same or another molecule of the same substance, is known as hydrogen bond. It is generally represented by dotted line.

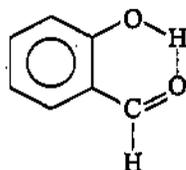
**Types of hydrogen bonding :** Hydrogen bonds are of two types :

(i) **Intermolecular hydrogen bonding :** When hydrogen bond is formed between two molecules of a compound, it is known as intermolecular hydrogen bonding. For example, in water molecule, intermolecular occurs.

(ii) **Intramolecular hydrogen bonding :** When hydrogen bond is formed within the same molecule, it is known as intramolecular hydrogen bonding. For example, in o-nitrophenol and o-hydroxybenzaldehyde intramolecular hydrogen bonding occurs.



o-Nitrophenol



o-Hydroxybenzaldehyde

**Nature of hydrogen bond :** Hydrogen bond is a directed electrostatic bond. The hydrogen only is capable of forming such a bond because of its small atomic size. After the removal of electron from the outermost shell, the proton can easily slip between two electronegative atoms. Hydrogen bond is formed by those elements which have small atomic size and are highly electronegative. This is because small atoms have strong electrostatic field around them. It is a weak bond. Its strength is 5-10% of a covalent bond.

**Effect of hydrogen bonding on properties of substances :** The physical properties of the substances are affected by hydrogen bonding. The compounds having intermolecular hydrogen bonding have comparatively high melting and boiling points because an additional amount of energy is required to break the hydrogen bonds. Moreover, under ordinary conditions, HF is a liquid, whereas HCl, HBr and HI are gases. Similarly,  $\text{H}_2\text{O}$  is a liquid whereas  $\text{H}_2\text{S}$  is a gas. This behaviour of HF and  $\text{H}_2\text{O}$  molecules can be explained on the basis of intermolecular hydrogen bonding. Organic compounds are generally insoluble in water, but the organic compounds containing  $-\text{OH}$  groups (e.g. alcohol, acid, carbohydrate, etc.) are soluble in water because these compounds can form hydrogen bonds with water molecules.



## SUMMARY

- Valency bond theory is based on the pairing and resultant neutralisation of opposite electron spins.
- Hybridization** : It is a phenomenon of mixing up of atomic orbitals of similar energies and formation of equivalent number of entirely new orbitals of identical shape and energy.
- The main types of hybridization are  $sp$ ,  $sp^2$ ,  $sp^3$  hybridization. The molecules  $BeF_2$ ,  $BCl_3$  and  $CH_4$  belong to these hybridizations, respectively.
- Coordination number** : The number of oppositely charged ions surrounding any particular ion in the crystal is known as coordination number. The coordination numbers of  $Na^+$  and  $Cl^-$  ions in  $NaCl$  crystal are 6, 6, respectively.
- Fajan's rule helps us to know the condition under which the electrovalency passes into covalency. This rule depends on large charge on the ions, small size of the cation, large size of the anion, nature of solvent and a cation with noble gas configuration etc.
- Hydrogen bond** : The attractive force that binds hydrogen atom of one molecule with electronegative atom of same or another molecule of the same substance is known as hydrogen bond.
- Hydrogen bonding is of two types, intermolecular and intramolecular bonding. These types produce different properties of the molecule.

## TEST YOURSELF

- Discuss valency bond theory and its limitations.
- Explain hybridization. How the shapes of molecules are related to the type of hybridization ?
- Write short notes on the following :  
(i) Coordination number (ii) Radius ratio rule (iii) Singlet bond
- Explain the structure of  $NaCl$  crystal.
- Explain polarization and polarizability of ions ? State Fajan's rules.
- With the help of Fajan's rule, explain which compound of each of the following pair is more covalent and why ?  
(i)  $CuO$  or  $CuS$  (ii)  $LiCl$  or  $NaCl$  (iii)  $AlCl_3$  or  $AlF_3$  (iv)  $SnCl_2$  or  $SnCl_4$
- Write a note on inert pair effect.
- What is an odd electron bond ? Discuss the characteristics of such a bond ?
- State and explain hydrogen bond. Discuss how hydrogen bonding effect the properties of substances by taking suitable examples.
- In benzene, each carbon atom is hybridized :  
(a)  $sp$  (b)  $sp^2$  (c)  $sp^3$  (d)  $dsp^2$
- Which of the following compounds has highest boiling point ?  
(a)  $CH_3Cl$  (b)  $CH_3OH$  (c)  $CH_3Br$  (d)  $CH_3I$
- Which one of the following ions has maximum polarizing power ?  
(a)  $Na^+$  (b)  $Mg^{2+}$  (c)  $Ca^{2+}$  (d)  $Al^{3+}$
- The hydrogen bonding is strongest in :  
(a)  $O-H \cdots S$  (b)  $S-H \cdots O$  (c)  $F-H \cdots F$  (d)  $F-H \cdots O$
- Explain why  $HF$  is a liquid, while  $HCl$  is a gas.
- Explain why  $H_2O$  is a liquid, while  $H_2S$  is a gas.
- Fill in the blanks :  
(i) The most covalent compound among  $NaCl$ ,  $MgCl_2$  and  $AlCl_3$  is .....  
(ii) The strongest hydrogen bond is formed between H and .....  
(iii) In  $NH_4^+$  ion, nitrogen atom is ..... hybridized.  
(iv) The maximum number of hydrogen bonds formed by each water molecule is .....

## ANSWERS

10. (b) 11. (b) 12. (d) 13. (c) 15. (i)  $AlCl_3$  (ii) F (iii)  $sp^3$  (iv) four.



**s-BLOCK AND p-BLOCK ELEMENTS****STRUCTURE**

- Periodic Discussion of Alkali Metals
- Diagonal Relationship of Lithium and Magnesium
- Abnormal Behaviour of Lithium
- Periodic Discussion of Alkaline Earth Metals
- Anomalous Behaviour of Beryllium
- Lithium Aluminium Hydride
- Periodic Discussion of III A Group
- Boron Hydrides
- Borax
- Periodic Discussion of IV A Group
- Periodic Discussion of V A Group
- Periodic Discussion of VI A Group
- Sodium Thiosulphate
- Periodic Discussion of VII A Group
- Abnormal Behaviour of fluorine
- Interhalogen Compounds
- Freon
- Teflon
- Student Activity
- Summary
- Test Yourself

**LEARNING OBJECTIVES**

After going this unit you will learn :

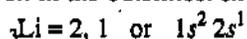
- Hydration of ions, hydration energy and behaviour of salts.
  - Similarity of lithium with magnesium.
  - Alkaline earth metals and alkali metals.
  - Beryllium and lithium aluminium hydride with their properties.
  - Boranes, diborane and borax with properties and their uses.
  - Nitrogen family, calcogens and interhalogen compounds.
- Preparation, properties and uses of freon and teflon.

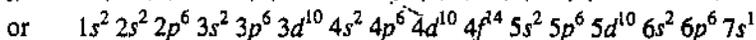
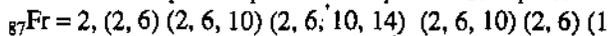
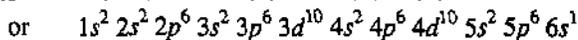
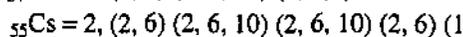
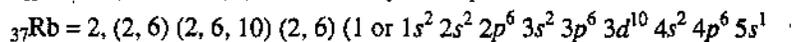
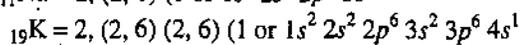
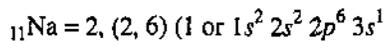
**s-BLOCK ELEMENTS****• 3.1. PERIODIC DISCUSSION OF ALKALI METALS**

The IA group of the periodic table contains lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr) having atomic numbers 3, 11, 19, 37, 55 and 87, respectively. The recently discovered element francium is radioactive and very little is known about its properties. These elements are called **alkali metals**, as they form strongly alkaline oxides and hydroxides. They show a marked similarity and regular gradation in their properties and thus, the position of these elements in the periodic table is justified.

**Similarity In Physical Properties**

(i) **Electronic configuration** : They all have similar electronic configuration, having one electron in the outermost shell.



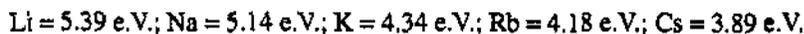


(ii) **Oxidation state** : These elements exhibit an oxidation state of +1. This is because they have only one electron in the outermost shell which they can easily lose. After removal of this electron, they acquire stable electronic configuration and the removal of more electrons is not easily possible.

(iii) **Atomic and ionic radii** : In general, atomic and ionic radii decrease in a period and increase in a group as the atomic number increases. Since each period starts with an alkali metal, the sizes of these elements are relatively large in their respective periods. The atomic and ionic radii of these elements increase from lithium to francium because of increase in the number of shells. The atomic and ionic radii of these elements are given below :



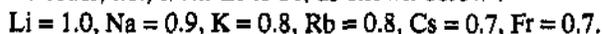
(iv) **Ionization potential** : The ionization potential of these elements is relatively low. This is because the atomic sizes of these elements are relatively large in their respective periods and increase from lithium to francium. Thus, the electrons of the outermost shell will be at a greater distance from the nucleus and their removal will be a little easier as the atomic number increases. Hence, the ionization potential of these elements decreases from lithium to francium. The first ionization potential of these elements is as follows :



The value of second ionization potential of these elements will be very high because the second electron is to be removed from the stable system.

(v) **Metallic character or electropositive character** : The metals have a tendency to lose electrons and to form positive ions. Thus, greater the tendency to lose the electrons, the greater will be metallic or electropositive character. The lower values of ionization potential indicate that these elements have a great tendency to lose electrons and thus, are strongly metallic or electropositive in character. This character increases from lithium to francium, as the atomic number increases.

(vi) **Electronegativity** : The electronegativity (the tendency of the atoms to attract electrons) of these elements is low, as these are highly electropositive. Since the electropositive character increases in a group as the atomic number increases, the electronegativity of these elements also decreases in the same order, i.e., from Li to Fr, as shown below :



(vii) **Polarizing power** : It is defined as the ratio of ionic charge to (ionic radius)<sup>2</sup>. In this group, the ionic radius increases from Li to Fr, whereas ionic charge remains the same. Therefore, polarizing power decreases in a group from Li to Fr.

When alkali metal cations approach towards an anion, the cation attracts the outermost electrons of the anion and repels the nucleus. Thus, the distortion or polarization of anion takes place resulting in the sharing of electrons between two oppositely charged ions, i.e., the bond becomes partly covalent in character. In general, the smaller cations polarize the anions more effectively than bigger ones. Therefore, the lithium salts are slightly covalent, whereas other alkali metal salts are ionic.

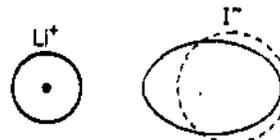
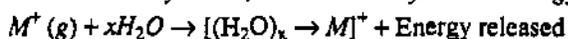


Fig. 1. Polarization of iodide ion by lithium ion.

(viii) **Hydration of ions and hydration energy** : The salts of alkali metals are ionic and soluble in water. The alkali metal cations are hydrated on dissolution in water. The process is exothermic and the energy released when one gram mole of an ion in the gaseous state is dissolved in water so as to make it hydrated, is known as hydration energy.



The electropositive character of metal has a tendency, to oppose the hydration of ions. Hence, a stronger electropositive ion will be hydrated to a lesser extent than the weaker electropositive ion. Since in a group, the electropositive character increases with the increase of atomic number, the degree of hydration and hence the hydration energy also decreases. Thus, in the alkali metals, lithium

ion is heavily hydrated, whereas caesium ion is least hydrated. Their hydration energies also decrease down the group, as shown below :

Alkali metal cation	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
Hydration energy in k. cal/mole	-121	-95	-76	-69	-62

The negative sign indicates the energy released.

(ix) **Flame colouration :** The alkali metals and their salts give characteristic colours to the flame.

Lithium	Sodium	Potassium	Rubidium	Caesium
Carmine red	Golden yellow	Pale-violet	Violet	Violet

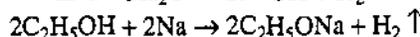
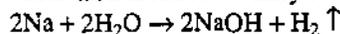
These metals when put to flame, the electrons are excited to the higher energy levels. These electrons return to their original positions with the emission of small energy which appears as visible light.

(x) **Melting and boiling points :** Their melting and boiling points are very low and decrease from lithium to francium as the atomic number increases.

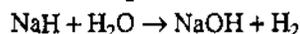
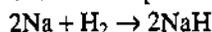
(xi) **Physical characteristics :** They are all silvery white metals. They are soft like wax and can be easily cut with a knife. They possess low specific gravity ranging from 0.53 to 1.90.

### Similarity in Chemical Properties

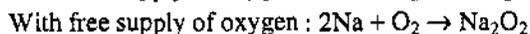
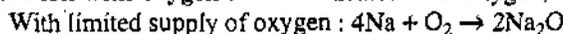
(i) **Action with water and alcohol :** They react with water and alcohol to give hydrogen.



(ii) **Action with hydrogen :** When heated with hydrogen, they form hydrides. These hydrides are electrovalent and are decomposed by water to give hydrogen.

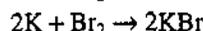
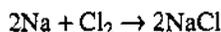


(iii) **Action with oxygen :** When heated with oxygen, they form oxides and peroxides.

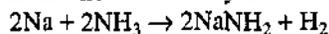


They dissolve in water to form strongly alkaline hydroxides.

(iv) **Action with halogens :** They react with halogens forming their halides, which are electrovalent compounds.

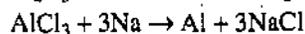
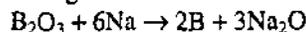


(v) **Action with ammonia :** They dissolve in liquid ammonia to give amides.



Sodamide

(vi) **Reducing property :** They have a great affinity for oxygen and halogens. Thus, they reduce oxides and chlorides to give free elements.



(vii) **Behaviour of salts :**

(a) They all form colourless salts unless derived from coloured anions.

(b) They are generally soluble in water.

(c) They are freely ionized in the aqueous solution or even in the fused state giving monovalent positive ions.

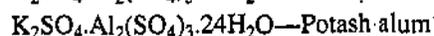
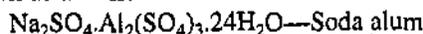
(d) The carbonates are very stable. They are soluble in water giving alkaline solution due to hydrolysis.



(e) The nitrates are sufficiently stable. On heating they decompose to form nitrites and oxygen.



(f) The sulphates of alkali metals combine with the sulphates of trivalent metals to form double salts, known as **alums**.



### Gradation in Properties

(i) Atomic weight, atomic radii, atomic volume and density increase, whereas melting point, boiling point, hardness, ionization potential and electronegativity decrease as the atomic number increases.

- (ii) The chemical reactivity of these elements increases as the atomic number increases.
- (iii) The strength of the hydroxides increases from LiOH to CsOH.
- (iv) The stability of carbonates and bicarbonates increases from Li to Cs.

### • 3.2. DIAGONAL RELATIONSHIP OF LITHIUM AND MAGNESIUM

Lithium differs from rest of the alkali metals and shows resemblance with the diagonally placed element, magnesium. The similarity of lithium with magnesium is due to the following reasons :

- (1) The atomic and ionic radii of lithium and magnesium are almost similar :

Atomic radii	Ionic radii
Li = 1.34Å	Li <sup>+</sup> = 0.60Å
Mg = 1.36Å	Mg <sup>2+</sup> = 0.65Å

- (2) The electropositive character of both is almost the same.
- (3) The electronegativity of both the elements is almost similar.

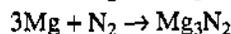
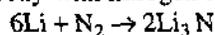
$$\text{Li} = 1.0, \text{Mg} = 1.2$$

- (4) The polarizing power, i.e.,  $\frac{\text{ionic charge}}{(\text{ionic radius})^2}$  of both elements is almost similar.

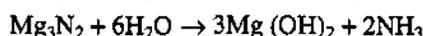
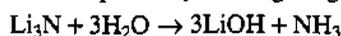
The main points, which indicate the similarity of lithium with magnesium and its difference from rest of the alkali metals, are :

- (i) Both lithium and magnesium are hard metals, whereas other alkali metals are soft.
- (ii) Both lithium and magnesium are less electropositive, whereas other alkali metals are strongly electropositive.
- (iii) Both react with water slowly, whereas other alkali metals react with water rapidly.
- (iv) Both form oxides on heating with oxygen or air, whereas other alkali metals form oxides without heating.

- (v) Both combine directly with nitrogen to form nitrides.

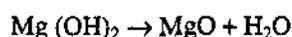


These nitrides are decomposed by water giving ammonia.



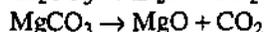
The other alkali metals do not combine with nitrogen at all.

- (vi) The oxides of lithium and magnesium are sparingly soluble in water and are less basic, whereas the oxides of other alkali metals are freely soluble in water and are strongly basic.
- (vii) The hydroxides of lithium and magnesium are weak bases and decompose on heating.



The other alkali metal hydroxides are strongly basic and are stable.

- (viii) The carbonates of lithium and magnesium decompose on heating.

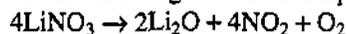


The carbonates of other alkali metals are very stable.

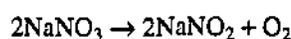
- (ix) The bicarbonates of lithium and magnesium are soluble in water, whereas those of other alkali metals are insoluble in water.

(x) The halides of both lithium and magnesium are soluble in the organic solvents such as alcohol and pyridine. The corresponding salts of other alkali metals are insoluble in organic solvents.

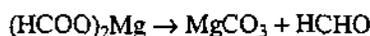
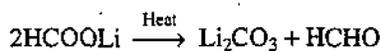
- (xi) The nitrates of lithium and magnesium decompose on heating giving NO<sub>2</sub> and O<sub>2</sub>.



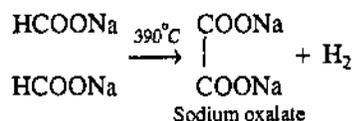
The nitrates of other alkali metals are sufficiently stable and decompose on heating to form nitrites and oxygen.



(xii) The formates of lithium and magnesium on heating give formaldehyde.



The formates of other alkali metals on heating form oxalates and hydrogen.



(xiii) The carbonates, oxalates, fluorides and phosphates of lithium and magnesium are sparingly soluble in water, whereas the corresponding salts of other alkali metals are freely soluble in water.

### • 3.3. ABNORMAL BEHAVIOUR OF LITHIUM

Lithium is present in the IA group along with sodium, potassium, rubidium, caesium and francium. They are all called alkali metals as they form strongly alkaline oxides and hydroxides. Lithium not only resembles with the elements of its own sub-group but also resembles with its diagonally related element, magnesium. Its position in the periodic table is justified because of the following facts :

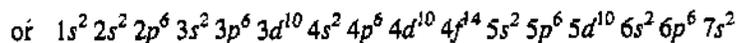
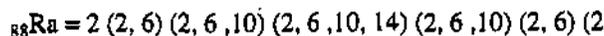
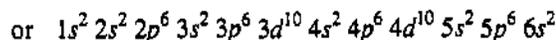
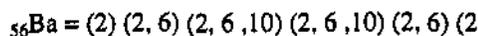
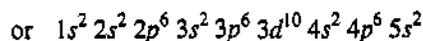
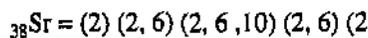
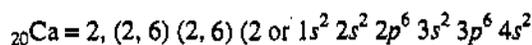
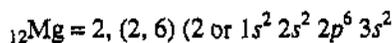
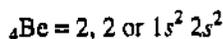
- (i) It resembles with the elements of its own sub-group.
- (ii) It shows regular gradation with the elements of its own sub-group.
- (iii) It resembles with the diagonally related element, magnesium.

### • 3.4. PERIODIC DISCUSSION OF ALKALINE EARTH METALS

The IIA group of the periodic table contains beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra) having atomic numbers 4, 12, 20, 38, 56 and 88, respectively. Radium is radioactive and has been studied separately. These elements are called *alkaline earth metals* after the principal members of group Ca, Sr and Ba. This is because the oxides of the elements were discovered earlier than the elements themselves. These oxides were alkaline in nature and existed on earth. Now, all the elements of the IIA group are known as *alkaline earth metals*. However, in the periodic discussion of this group, Ca, Sr and Ba have been considered as one family. They show a marked similarity and regular gradation in their properties and thus, the position of these elements in the periodic table is justified.

#### Similarity In Physical Properties

(i) **Electronic configuration :** They all have similar electronic configuration having two electrons in the outermost shell.



(ii) **Atomic and ionic radii :** The atoms of these elements are smaller than those of the corresponding alkali metals. This is due to the increased nuclear charge which attracts the electrons more towards the nucleus. The atomic and ionic radii increase from beryllium to radium. The values are as follows :

	Be	Mg	Ca	Sr	Ba	Ra
Atomic radii	0.90Å	1.36Å	1.74Å	1.92Å	1.98Å	—
Ionic radii of M <sup>2+</sup> ions	0.31Å	0.65Å	0.99Å	1.13Å	1.35Å	1.50Å

(iii) **Ionization potential** : The ionization potential of these elements is low just like alkali metals. This is because their atoms are smaller than those of alkali metals. The electrons are attracted more strongly by the nucleus and hence, the energy required to remove the first electron is greater than for alkali metals. After the removal of first electron, the effective nuclear charge is increased and, therefore, the energy required to remove another electron is nearly double. The values of first and second ionization potential of these elements decrease from Be to Ba for the reasons already discussed.

(iv) **Oxidation state** : The lower value of first ionization potential, as compared to second, indicates that these elements should form monovalent ions rather than divalent ions. But in actual practice, they form divalent ions. This is because of the fact that M<sup>2+</sup> ions are heavily hydrated and a large amount of energy known as *hydration energy* is liberated in the process. This energy is more than the energy required for the removal of second electron.

(v) **Metallic character or electropositive character** : These elements have a great tendency to lose electrons. Thus, these elements are strongly electropositive, although less than the alkali metals. This character increases from beryllium to radium as the atomic number increases.

(vi) **Electronegativity** : The electronegativity of these elements is low as these are electropositive. The values decrease as the atomic number increases.

Alkaline earth metals	Be	Mg	Ca	Sr	Ba	Ra
Electronegativity	1.5	1.2	1.0	1.0	0.9	0.9

(vii) **Polarizing power** : It is defined as *the ratio of ionic charge to (ionic radius)<sup>2</sup>*. In this group, the ionic radius increases from Be to Ra, whereas ionic charge remains the same. Therefore, polarizing power decreases from beryllium to radium. In general, smaller atoms polarize the anions more effectively than bigger ones. Therefore, beryllium has a tendency to form covalent compounds.

(viii) **Hydration of ions and hydration energy** : The ions of these elements are more heavily hydrated than those of the alkali metal ions. This is because the hydration energies of these ions are larger than those of alkali metal ions and decrease from Be<sup>2+</sup> to Ba<sup>2+</sup> ion.

M <sup>2+</sup> ions	Be <sup>2+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>
Hydration energy	-570	-460	-395	-355	-305

The negative sign indicates the energy released.

(ix) **Flame colouration** : The alkaline earth metals and their salts give characteristic colour to the flame.

Ca : brick red, Sr : crimson, Ba : apple green, Ra : carmine red.

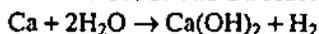
Beryllium and magnesium do not give any colour to the flame.

(x) **Hardness** : These metals are much harder than alkali metals and their hardness decreases as the atomic number increases.

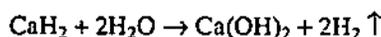
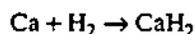
(xi) **Physical characteristics** : They are silvery white metals. They are sufficiently soft. They possess low specific gravity and low melting point, although higher than that of alkali metals.

#### Similarity in chemical properties

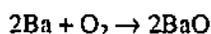
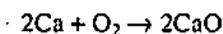
(i) **Action with water** : Ca, Sr and Ba react with water giving H<sub>2</sub>.



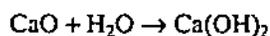
(ii) **Action with hydrogen** : When heated with hydrogen, they form hydrides. These hydrides are decomposed by water to give H<sub>2</sub>.



(iii) **Action with oxygen** : They burn in oxygen to form ionic oxides.



These oxides dissolve in water to form strongly alkaline hydroxides.



(iv) **Action with covalent halides :** Corresponding hydrides are formed.



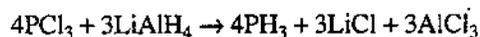
Silane



Stannane



Diborane



Phosphine

### [III] Uses

Lithium aluminium hydride is used.

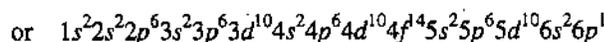
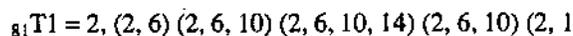
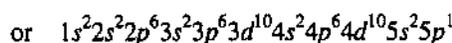
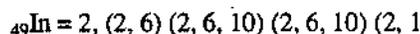
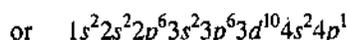
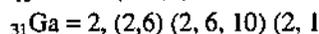
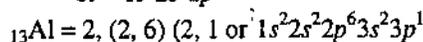
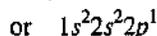
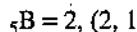
(i) As a reducing agent in organic chemistry.

(ii) In the preparation of a number of inorganic hydrides such as  $\text{B}_2\text{H}_6$ ,  $\text{SiH}_4$ ,  $\text{SnH}_4$ ,  $\text{PH}_3$  etc., which are otherwise difficult to prepare.

## p-BLOCK ELEMENTS

### • 3.7. PERIODIC DISCUSSION OF III A GROUP

Boron is present in the III A group of the periodic table along with aluminium, gallium, indium and thallium. These are all *p*-block elements having  $ns^2 np^1$  configuration in their outermost shell.



These elements may be divided into two classes due to the difference in the electronic configuration of their penultimate shells. Boron and aluminium have 2 and 8 electrons in their penultimate shell, *i.e.*, they have inert gas type of electronic configuration of their penultimate shell. The other elements gallium, indium and thallium have 18 electrons in their penultimate shell, *i.e.*, they have pseudo inert gas type of electronic configuration. This difference in the electronic configuration is responsible for the difference in the properties of both the classes of elements and also of boron and aluminium. Although boron and aluminium are the typical elements of the group, yet they do not show much resemblance. This is due to the big difference in their size and ionization potential. Boron also resembles with silicon, the element diagonally related to it.

### • 3.8. BORON HYDRIDES

Although boron does not combine directly with hydrogen, yet several hydrides of boron are known. These are also called as **boranes** by analogy with alkanes. These are divided into two series, *viz.*,  $\text{B}_n\text{H}_{n+4}$  and a less stable series,  $\text{B}_n\text{H}_{n+6}$ .

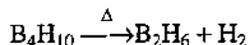
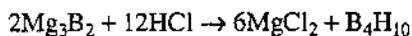
$\text{B}_n\text{H}_{n+4}$	$\text{B}_n\text{H}_{n+6}$
$\text{B}_2\text{H}_6$ —Diborane (Boro ethane)	$\text{B}_4\text{H}_{10}$ —Tetraborane (Boro butane)
$\text{B}_5\text{H}_9$ —Pentaborane-9 (stable)	$\text{B}_5\text{H}_{11}$ —Pentaborane-11 (unstable)
$\text{B}_6\text{H}_{10}$ —Hexaborane-10 (stable)	$\text{B}_6\text{H}_{12}$ —Hexaborane-12 (unstable)
$\text{B}_8\text{H}_{12}$ —Octaborane-12	$\text{B}_9\text{H}_{15}$ —Nonaborane
$\text{B}_{10}\text{H}_{14}$ —Decaborane-14 (stable)	$\text{B}_{10}\text{H}_{16}$ —Decaborane-16 (unstable)

The simplest boron hydride  $BH_3$  is unknown. These hydrides have been studied recently by Stock and his co-workers. Among these, the diborane has been studied more than others. The chemistry of higher boranes is similar to that of diborane.

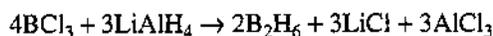
### [I] Diborane, $B_2H_6$

#### [I] Preparation :

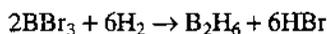
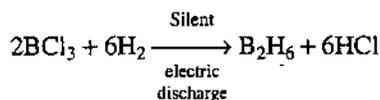
(i) By the action of dil. HCl on magnesium boride : A mixture of boron hydrides, mainly tetraborane, is formed which, on heating, breaks into diborane and hydrogen.



(ii) By the action of lithium aluminium hydride on boron trichloride in the presence of ether.

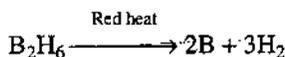


(iii) By passing silent electric discharge at 10 mm pressure through a mixture of boron trichloride or tribromide and excess of hydrogen.

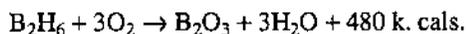


#### [II] Properties :

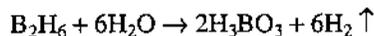
(i) Diborane is a colourless gas which is stable only at low temperatures. It changes to higher boranes even at ordinary temperature. It decomposes into boron and hydrogen at red heat.



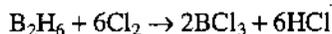
(ii) Action with oxygen : Diborane burns in oxygen, liberating a large amount of energy.



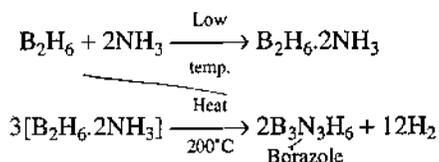
(iii) Hydrolysis : Diborane is readily hydrolysed to form boric acid.



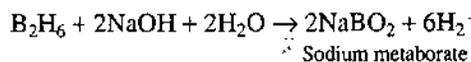
(iv) Action with chlorine : Boron trichloride is formed.



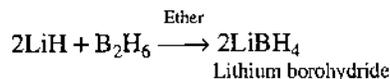
(v) Action with ammonia : At low temperatures, an addition product  $B_2H_6 \cdot 2NH_3$  is obtained which, on heating at  $200^\circ C$ , forms borazole (inorganic benzene).



(vi) Action with alkalis : Diborane dissolves in conc. alkalis to form metaborate.



(vii) Action with lithium hydride in ethereal solution : Lithium borohydride is formed.



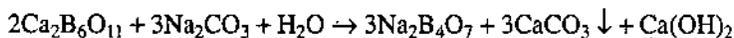
#### [III] Uses

The hydrides of boron are used as fuel for rockets because of their very high energy/weight ratio.

### • 3. 9. BORAX, $Na_2B_4O_7$

#### [I] Preparation

(i) From colemanite : The finely powdered mineral is boiled with calculated quantity of sodium carbonate solution.



The precipitate of calcium carbonate is removed by filtration and borax is crystallized from the filtrate.

(ii) **From native borax or razorite :** The finely powdered mineral is treated with hot water which dissolves borax, leaving behind the insoluble impurities. The solution is now concentrated and cooled when the crystals of borax are deposited.

(iii) **From boric acid :** Borax may also be obtained by neutralizing a solution of the acid by soda ash.



### [II] Properties

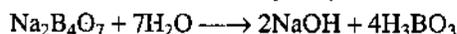
(1) It is a white crystalline solid. It exists in three forms :

(i) *Prismatic borax* ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) : It is the ordinary form of borax. It is obtained when a solution of the salt is crystallized at ordinary temperature.

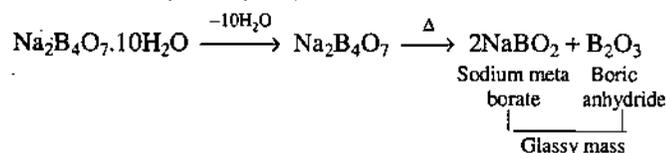
(ii) *Octahedral borax* ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ ) : It is obtained when a solution of the salt is crystallized above  $60^\circ\text{C}$ .

(iii) *Borax glass* ( $\text{Na}_2\text{B}_4\text{O}_7$ ) : It is obtained by heating ordinary form of borax above its melting point until all the water of crystallization is lost. It is a colourless glassy substance. It absorbs moisture from the atmosphere and slowly changes into ordinary form.

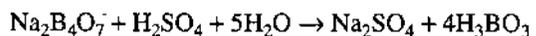
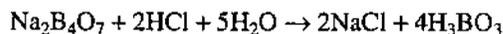
(2) **Basic nature :** Borax is sparingly soluble in cold water but is readily soluble in hot water. Its aqueous solution is alkaline due to hydrolysis.



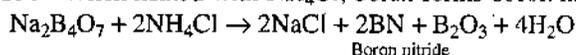
(3) **Action of heat :** On heating above its melting point, borax loses its water of crystallization and swells up to a white porous mass. On further heating, it melts into a liquid which then solidifies to form a transparent glassy mass.



(4) **Action of acids :** Borax reacts with conc. HCl or conc.  $\text{H}_2\text{SO}_4$  to form sparingly soluble boric acid.



(5) **Action with  $\text{NH}_4\text{Cl}$  :** When heated with  $\text{NH}_4\text{Cl}$ , borax forms boron nitride.



### [III] Uses

Borax is used :

(i) In borax bead test for the detection of basic radicals. (ii) In the manufacture of enamels and glazes for pottery. (iii) In making optical glass and boro-silicate glassware. (iv) As a flux in metallurgy. (v) As a preservative for food. (vi) In the manufacture of washing powders and soaps. (vii) In leather and match industries.

## • 3.10. PERIODIC DISCUSSION OF IV A GROUP

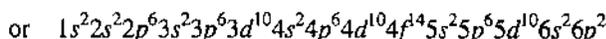
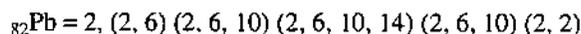
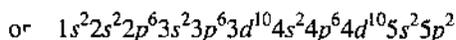
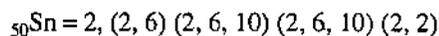
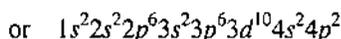
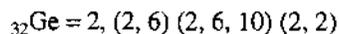
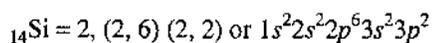
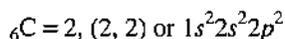
The elements carbon, silicon, germanium, tin and lead are present in the IV A group of the periodic table having atomic numbers 6, 14, 32, 50 and 82 respectively. These are *p*-block elements and except germanium, all are abundant. Carbon and silicon are called typical elements of the group. This group occupies a central position in the periodic table, three groups on either side. The elements placed to the left are metals and elements to the right are non-metals. In the elements of this group, both the electropositive and electronegative characters are equally developed and thus, it may be considered as a separating group between metals and non-metals. In general, carbon, the first element of the group, differs from rest of the elements of the group because of the following facts :

- (i) Smaller atomic size.
- (ii) Higher electronegativity.
- (iii) Non-availability of empty *d*-orbitals in its valency shell.
- (iv) Tendency of multiple bond formation, i.e.,  $\text{C}=\text{C}$ ,  $\text{C}\equiv\text{C}$ ,  $\text{C}=\text{O}$ ,  $-\text{C}\equiv\text{N}$  etc.
- (v) Tendency to form long chains (catenation).

Carbon and silicon have only *s*- and *p*-orbitals, whereas the other elements have complete *d*-orbitals in their penultimate shells. Thus, due to the difference in the electronic configuration, carbon and silicon differ from one another and also from rest of the elements of the group. The position of these elements in the periodic table is justified because of the following facts :

### Similarity in Physical Properties

(i) **Electronic configuration :** They all have similar electronic configurations having four electrons in the outermost shell.



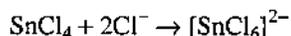
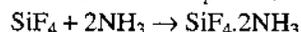
(ii) **Valency :** All these elements are tetravalent. The ionization potentials of these elements are very high, therefore, they do not form stable  $M^{4+}$  ions. On the other hand, the electronegativities of these elements are not so low, therefore, they do not normally form  $M^{4-}$  ions. However, carbon forms  $C_2^{2-}$  ions in metallic carbides such as  $CaC_2$ . Thus, these elements show a covalency of four and form compounds by sharing of electrons.

The last two elements Sn, Pb also form  $M^{2+}$  ions due to inert pair effect.

(iii) **Oxidation state :** These elements have, in general, an oxidation state of +4. However, the last two elements Sn and Pb also show +2 oxidation state due to inert pair effect. Carbon, however, shows a number of other oxidation states as -4, -2, 0 and +2 in its compounds  $CH_4$ ,  $CH_3Cl$ ,  $CH_2Cl_2$  and  $CHCl_3$ , respectively.

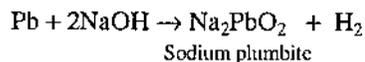
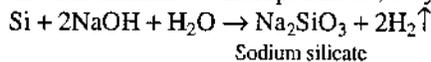
(iv) **Formation of complexes :** Except carbon, they all form complex compounds. This is because in the tetra covalent compounds of carbon ( $CH_4$ ,  $CCl_4$ ), no vacant orbitals are available for coordination.

In the tetra covalent compounds of remaining elements of the group, vacant *d*-orbitals are available in the outermost shell. Thus, these compounds may accept lone pair of electrons from anions or neutral molecules and form complex compounds.

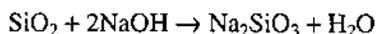
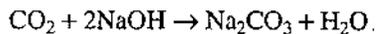


(v) **Allotropy :** Except lead, they all show allotropy *i.e.*, they exist in more than one form. Thus, carbon occurs in two crystalline forms, diamond and graphite and a number of amorphous forms such as coal, coke, charcoal etc. Silicon exists in two forms : crystalline and amorphous. Germanium is also found in two crystalline forms. Tin occurs in three forms : grey tin, white tin and rhombic tin.

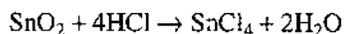
(vi) **Action with alkalis :** Except carbon, they all react with alkalis to form hydrogen.

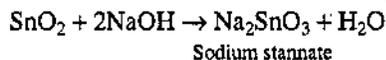


(vii) **Formation of oxides :** They all form oxides of the general formula,  $MO_2$ . The dioxides of carbon and silicon are acidic and dissolve in alkalis to form salts.



The dioxides of remaining elements are amphoteric and dissolve both in acids and alkalis to form salts.

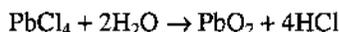
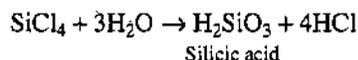




They also form lower oxides of the general formula,  $\text{MO}$ . These oxides except those of silicon and germanium are quite stable.

(viii) **Formation of hydrides** : They all form covalent hydrides of the general formula,  $\text{MH}_4$  ( $\text{CH}_4$ ,  $\text{SiH}_4$ ,  $\text{GeH}_4$ ,  $\text{SnH}_4$ ,  $\text{PbH}_4$ ). They are all colourless gases. The hydrides of all other elements are unstable except those of carbon.

(ix) **Formation of halides** : They all form tetrahedral covalent halides. The tetra chlorides are generally volatile liquids at ordinary temperature and their stability decreases as we move down the group. Except  $\text{CCl}_4$ , all are readily hydrolysed by water.



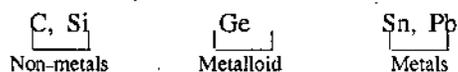
Carbon, silicon and germanium also form compounds of the general formula,  $\text{M}_4\text{ICl}_3$ . Tin and lead, however, do not form such compounds but form lower chlorides,  $\text{SnCl}_2$ ,  $\text{PbCl}_2$ .

(x) **Formation of sulphides** : Except lead which forms monosulphide, they all form di-sulphides of the general formula,  $\text{MS}_2$  when heated with sulphur.

### Gradation in properties

(1) **Physical properties** : Atomic weight, atomic radius, atomic volume, density increase, whereas ionization potential, melting and boiling points decrease from carbon to lead.

(2) **Electropositive character or metallic character** : It gradually increases as the atomic number increases. Thus, carbon and silicon are non-metals, germanium is a metalloid, whereas tin and lead are true metals.



(3) **Nature of oxides** : The acidic character of dioxides decreases, whereas basic character increases from carbon to lead. The dioxides of carbon and silicon are acidic, whereas those of rest elements are amphoteric in character.

(4) **Nature of hydrides** : The stability of hydrides decreases down the group. This is indicated by the decomposition temperature of  $\text{MH}_4$  hydrides.

Hydrides	$\text{CH}_4$	$\text{SiH}_4$	$\text{GeH}_4$	$\text{SnH}_4$	$\text{PbH}_4$
Decomposition temperature	800°C	450°C	285°C	150°C	0°C

(5) **Nature of halides** : The stability of the tetrahalides decreases as we move down the group. Thus,  $\text{CCl}_4$  is most stable and  $\text{PbCl}_4$  is least stable.

### • 3.11. PERIODIC DISCUSSION OF V A GROUP

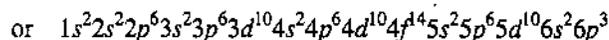
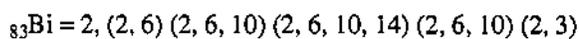
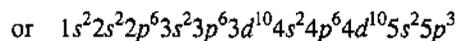
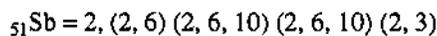
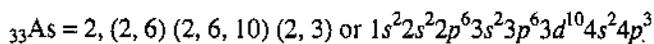
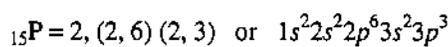
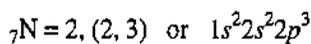
The elements **nitrogen (N)**, **phosphorus (P)**, **arsenic (As)**, **antimony (Sb)** and **bismuth (Bi)** are present in the VA group of the periodic table having atomic numbers 7, 15, 33, 51 and 83, respectively. They are also called members of the **nitrogen family** as nitrogen is the most important element among these. These are *p*-block elements having configuration  $ns^2 np^3$  of the outermost shell. Being the elements of the same group, they show many similar properties with regular gradation in their properties. However, nitrogen, the first element of the group, differs from rest of the elements of the group because of the following facts :

- (i) Smaller atomic size.
- (ii) Higher electronegativity.
- (iii) Non-availability of empty *d*-orbitals in its valency shell.
- (iv) Tendency of multiple bond formation, i.e.,  $\text{C} \equiv \text{N}$ ,  $\text{N} \equiv \text{N}$  etc.

The position of these elements in the periodic table is justified because of the following facts:

#### Similarity in Physical Properties

(i) **Electronic configuration** : They all have similar electronic configuration having  $ns^2 np^3$  electrons in the outermost shell.



In the atoms of these elements, the  $p$ -orbitals of their respective outershells are only half filled. Hence, these elements are fairly stable and not so reactive.

(ii) **Valency** : The common valencies of these elements are 3 and 5. The atoms of these elements have two paired  $s$ -electrons and three unpaired  $p$ -electrons. Thus, these elements can form three covalent bonds by using the three unpaired  $p$ -electrons. However, nitrogen, because of its smallest atomic size and highest electronegativity in the group, can also accept three electrons from highly electropositive elements to form  $\text{N}^{3-}$  ions which is not the case with any other element of the group.

(iii) **Oxidation states** : The atoms of these elements have  $ns^2 np_x^1 p_y^1 p_z^1$  electronic configuration of their outermost shells. Thus, these elements can have two positive oxidation states +3 and +5. The +3 oxidation state arises when only three  $p$ -electrons are involved whereas +5 oxidation state arises when both  $s$ - and  $p$ -electrons are involved in the chemical bonding. In addition, nitrogen also shows +1, +2 and +4 oxidation states in its compounds with oxygen,  $\text{N}_2\text{O}$ ,  $\text{NO}$  and  $\text{NO}_2$  respectively.

Except bismuth, all the elements also show -3 oxidation state. Nitrogen also shows oxidation states -1 and -2 in the compounds  $\text{NH}_2\text{OH}$  and  $\text{NH}_2\text{—NH}_2$ , respectively.

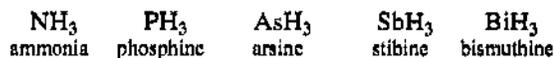
(iv) **Occurrence** : Except nitrogen, which occurs in free state also, all occur in combined state only.

(v) **Allotropy** : Except bismuth, all the elements show allotropy. Thus, two solid forms of nitrogen, known as  $\alpha$ -nitrogen and  $\beta$ -nitrogen, have been reported. Phosphorus occurs in a number of allotropic forms such as yellow or white phosphorus, red phosphorus, violet phosphorus, scarlet phosphorus,  $\alpha$ -black phosphorus and  $\beta$ -black phosphorus. Arsenic is found in grey, yellow and black allotropic forms. Antimony also exists in three different forms, e.g., metallic form, yellow form and explosive antimony.

(vi) **Formation of oxides** : They all form oxides of the general formula  $\text{M}_2\text{O}_3$  and  $\text{M}_2\text{O}_5$ . The trioxides of nitrogen and phosphorus are acidic, those of arsenic and antimony are amphoteric while that of bismuth is basic in character. The pentoxides are acidic in each case. Nitrogen forms some other oxides also as  $\text{N}_2\text{O}$ ,  $\text{NO}$  and  $\text{NO}_2$ .

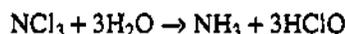
(vii) **Formation of oxy acids** : They all form oxy acids. Thus, nitrogen forms a number of oxy acids such as  $\text{H}_2\text{N}_2\text{O}_2$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$  and  $\text{HNO}_4$ . Phosphorus also forms a large number of oxyacids such as  $\text{H}_3\text{PO}_2$ ,  $\text{H}_3\text{PO}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_4\text{P}_2\text{O}_7$ ,  $\text{H}_4\text{P}_2\text{O}_6$ ,  $\text{HPO}_3$ ,  $\text{H}_3\text{PO}_5$ ,  $\text{H}_4\text{P}_2\text{O}_8$ . Arsenic forms two oxyacids - arseneous acid,  $\text{H}_3\text{AsO}_3$  and arsenic acid,  $\text{H}_3\text{AsO}_4$ . Antimony also forms two oxyacids - antimonic acid,  $\text{H}_3\text{SbO}_4$  and pyro antimonic acid,  $\text{H}_4\text{Sb}_2\text{O}_7$ . Bismuth gives only one oxy acid - meta bismuthic acid,  $\text{HBiO}_3$ .

(viii) **Formation of hydrides** : They all form volatile hydrides of the general formula  $\text{MH}_3$ .

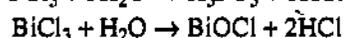
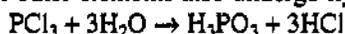


All these hydrides are colourless gases. Except ammonia, they are poisonous.

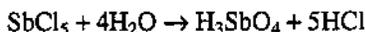
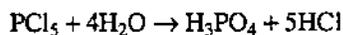
(ix) **Formation of halides** : They all form trihalides of the general formula  $\text{MX}_3$ . These halides are covalent and have a tetrahedral structure.  $\text{NF}_3$  is a stable gas while  $\text{NCl}_3$  is an explosive compound and is readily hydrolysed.



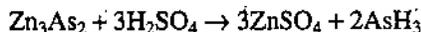
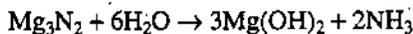
The trihalides of other elements also undergo hydrolysis.



Phosphorus, arsenic and antimony are also known to form penta halides of the general formula  $\text{MX}_5$ . Nitrogen does not form penta halide due to absence of vacant  $d$ -orbitals, and bismuth does not form penta halide due to inert pair effect. These penta halides have trigonal bipyramidal structure and are also hydrolysed by water.



(x) **Combination with metals:** They all combine with the metals like alkali metals, calcium, magnesium and zinc etc. to form nitrides, phosphides, arsenides, antimonides and bismuthides. These compounds produce hydrides with water or dilute acids.



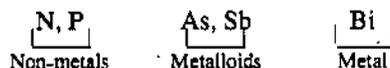
### Gradation in Properties :

(i) Atomic weight, atomic radii, atomic volume, density and boiling point gradually increase whereas electronegativity, ionization potential decrease as the atomic number increases.

(ii) The melting point increases from nitrogen to arsenic and then decreases from arsenic to bismuth.

(iii) Nitrogen is a colourless gas, phosphorus is a soft white solid and the elements after that are harder and harder solids.

(iv) The metallic character or electropositive character increases as the atomic number increases. Thus, nitrogen and phosphorus are typical non-metals, arsenic and antimony are metalloids, whereas bismuth is a true metal.



## • 3.12. PERIODIC DISCUSSION OF VI A GROUP

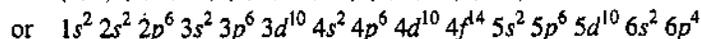
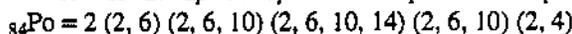
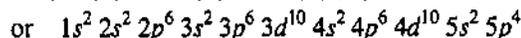
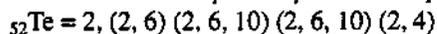
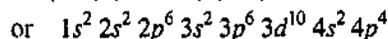
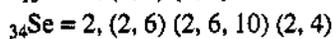
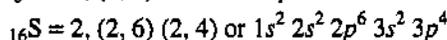
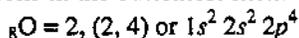
The elements oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po) are present in the VI A group of the periodic table having atomic numbers 8, 16, 34, 52 and 84, respectively. These are  $p$ -block elements having the configuration  $ns^2 np^4$  ( $ns^2 np_x^2 p_y^1 p_z^1$ ) of the outermost shell. These elements are known as **chalcogens**, *i.e.*, ore forming elements. This is, because many metallic compounds of these elements are found in nature. Oxygen is the most abundant and constitutes 46.6% of the earth crust. Polonium is radioactive and very little is known about its properties. Being the elements of the same group, they show many similar properties with a regular gradation in their properties. However, oxygen, the first element of the group, differs from rest of the elements of the group because of the following facts :

1. Smaller atomic size.
2. Higher electronegativity.
3. Non-availability of empty  $d$ -orbitals in the valency shell.
4. Tendency of multiple bond formation, *i.e.*,  $\text{O}=\text{O}$ ,  $\text{O}=\text{C}=\text{O}$ .

The position of these elements in the periodic table is justified because of the following facts.

### Similarity in Physical Properties

(i) **Electronic configuration:** They all have similar electronic configuration having  $ns^2 np^4$  electrons in the outermost shell.

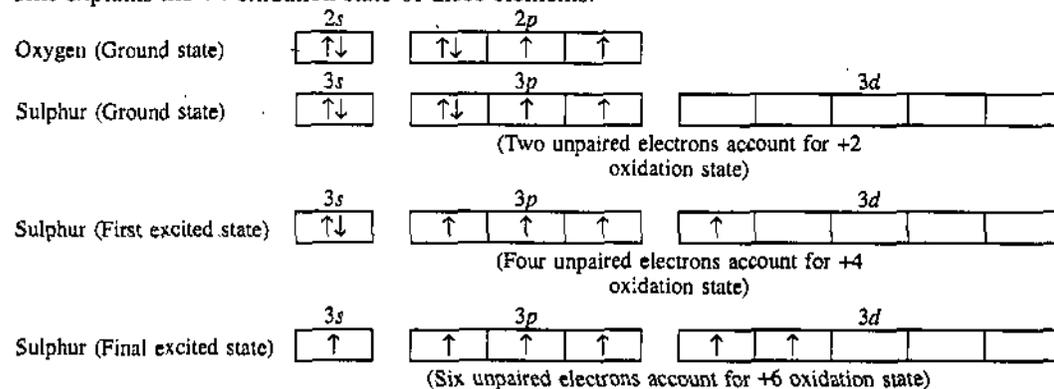


(ii) **Oxidation state:** The atoms of these elements have  $ns^2 np_x^2 p_y^1 p_z^1$  configuration of their outermost shells. Thus, these elements have a tendency to gain or share two electrons in order to attain noble gas configuration. Oxygen, because of its high electronegativity, will prefer to complete

its octet by gaining two electrons. Even if the octet is completed by sharing of electrons, the oxidation state of oxygen will be  $-2$  except in  $F_2O$  in which it has an oxidation state  $+2$ .

The electronegativities of the remaining elements of the group are, however, low. Hence, the compounds of these elements, even with the most electropositive elements, are never more than 50% ionic. Thus, in the case of S, Se and Te, there is much less possibility of the formation of dinegative ions.

Oxygen, in its valency shell, contains only *s*- and *p*-orbitals, whereas the remaining elements contain vacant *d*-orbitals also in their valency shells. In the ground state, there are only two unpaired electrons which may be used for bond formation. In the excited state, one of the *p*-electrons may jump to the vacant *d*-orbitals, thus producing four unpaired electrons available for bond formation. This explains the  $+4$  oxidation state of these elements.

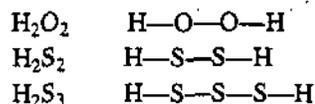


In the final excited state, one of the *s*-electrons may also jump to the vacant *d*-orbitals, thus producing six unpaired electrons available for bond formation. This explains the  $+6$  oxidation state of these elements.

(iii) **Allotropy** : They all show allotropy. Thus, oxygen occurs in two non-metallic forms – oxygen and ozone. Sulphur is found in a number of allotropic forms, all of which are non-metallic. These forms are rhombic or  $\alpha$ -sulphur, monoclinic or  $\beta$ -sulphur, plastic or  $\gamma$ -sulphur, colloidal or  $\delta$ -sulphur,  $\lambda$ -sulphur and  $\mu$ -sulphur. Selenium occurs in two forms – red form (non-metallic) and grey form (metallic). Tellurium has two forms – non-metallic and more stable metallic form. Polonium also exists in two forms known as  $\alpha$ -form and  $\beta$ -form, both of which are metallic.

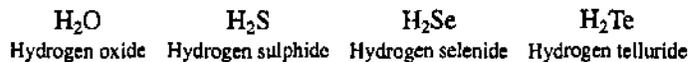
(iv) **Atomicity** : All the elements are polyatomic. Thus, oxygen molecule is diatomic, whereas the molecules of other elements are more complex. Sulphur and selenium occur as octatomic molecules  $S_8$  and  $Se_8$  with puckered ring structures.

(v) **Catenation** : All the elements of the group show the property of catenation, *i.e.*, they have a tendency to form chains of identical atoms. This tendency is most marked in sulphur and it decreases down the group. Thus, chains of sulphur atoms are present in polysulphides, polythionic acids, sulphanes and in  $S_8$  molecule. Oxygen gives fairly stable polyoxides similar to polysulphides given by sulphur.



The elements Se and Te form chains and rings only in their elemental state.

(vi) **Formation of hydrides** : They all combine with hydrogen to form hydrides of the general formula  $H_2X$ .



The hydride of oxygen, *i.e.*,  $H_2O$  is a colourless, odourless and non-poisonous liquid, whereas the hydrides of the remaining elements are colourless gases with an unpleasant smell and are poisonous.

(vii) **Formation of oxides and oxyacids** : The elements sulphur, selenium and tellurium combine with oxygen to give oxides of the general formula  $XO_2$  and  $XO_3$ . These oxides are acidic and dissolve in water to form the corresponding oxy acids of the general formula  $H_2XO_3$  and  $H_2XO_4$  respectively.

	Dioxide	Corresponding oxy acid	Trioxide	Corresponding oxy acid
Sulphur	SO <sub>2</sub>	H <sub>2</sub> SO <sub>3</sub> Sulphurous acid	SO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>
Selenium	SeO <sub>2</sub>	H <sub>2</sub> SeO <sub>3</sub> Selenous acid	SeO <sub>3</sub>	H <sub>2</sub> SeO <sub>4</sub>
Tellurium	TeO <sub>2</sub>	H <sub>2</sub> TeO <sub>3</sub> Tellurous acid	TeO <sub>3</sub>	H <sub>2</sub> TeO <sub>4</sub>

(viii) **Formation of halides** : These elements form a number of halides with the halogens which are more electronegative. Oxygen combines with the halogens to a lesser extent and the compounds like F<sub>2</sub>O, F<sub>2</sub>O<sub>2</sub>, Cl<sub>2</sub>O, Cl<sub>2</sub>O<sub>7</sub>, Br<sub>2</sub>O, BrO<sub>2</sub>, I<sub>2</sub>O<sub>4</sub>, I<sub>2</sub>O<sub>5</sub> are unstable.

Sulphur, selenium and tellurium form several types of halides like hexachlorides, tetrahalides, dihalides and monohalides.

(ix) **Combination with carbon** : All the elements of the group combine with carbon to form compounds, e.g., CO<sub>2</sub>, CS<sub>2</sub>, CSe<sub>2</sub> and CTe<sub>2</sub>. The monoxide and mono sulphide of carbon, e.g., CO and CS are also known. All these compounds are covalent in nature.

(x) **Combination with metals** : They all combine with many metals like sodium, copper, zinc, iron etc. to form their oxides, sulphides, selenides and tellurides, respectively. These compounds have typical ionic crystal structure.

### Gradation in Properties

(i) Atomic weight, atomic radius, atomic volume, specific gravity, melting and boiling point gradually increase, whereas electronegativity, ionization potential decrease as the atomic number increases.

(ii) The metallic character or electropositive character increases as the atomic number increases. Thus, oxygen and sulphur are non-metals, selenium and tellurium are metalloids, whereas polonium is definitely a metal.

(iii) The chemical reactivity of these elements decreases as the atomic number increases.

(iv) **Nature of hydrides.**

(a) **Stability** : The stability of the hydrides decreases with the increase in molecular weight. Thus, water dissociates at about 2000°C, H<sub>2</sub>S at 400–600°C, H<sub>2</sub>Se at about 150°C, whereas H<sub>2</sub>Te decomposes even at ordinary temperature.

(b) **Volatility** : The volatility increases markedly from H<sub>2</sub>O to H<sub>2</sub>S and then decreases. This is indicated from their boiling points.

H <sub>2</sub> O	H <sub>2</sub> S	H <sub>2</sub> Se	H <sub>2</sub> Te
100°C	-61°C	-41.5°C	-2°C

The abnormally low volatility, i.e., high boiling point of water is due to the association of its molecules through hydrogen bonding.

(c) **Acidic character** : Except water, which is neutral, the aqueous solutions of remaining hydrides are weakly acidic. The acidic strength increases from H<sub>2</sub>S to H<sub>2</sub>Te.

(d) **Reducing character** : Except water, all the hydrides of the group are reducing agents. The reducing character increases from H<sub>2</sub>S to H<sub>2</sub>Te.

(e) **Poisonous character** : Except water, all the hydrides are poisonous. The poisonous character increases from H<sub>2</sub>S to H<sub>2</sub>Te.

(v) **Nature of oxy-acids** : The strength and stability of oxy-acids decrease down the group. Thus, H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> are very strong acids and are very stable, whereas H<sub>2</sub>TeO<sub>3</sub>, H<sub>2</sub>TeO<sub>4</sub> are weak acids and decompose on warming.

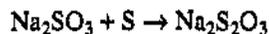
### • 3.13. SODIUM THIOSULPHATE, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O

#### [I] Preparation

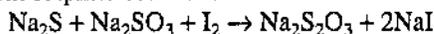
(i) By boiling sulphur with caustic soda solution.



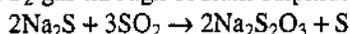
(ii) By boiling sodium sulphite solution with powdered sulphur till the solution is no more alkaline.



(iii) **From Spring's reaction** : By adding calculated quantity of iodine to a mixture of sodium sulphide and sodium sulphite solutions.



(iv) By passing  $\text{SO}_2$  gas through sodium sulphide solution.



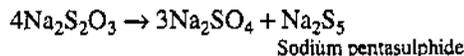
(v) Commercially, sodium thiosulphate is prepared by passing  $\text{SO}_2$  gas through a mixture of sodium sulphide and sodium carbonate solutions.



### [III] Properties

Sodium thiosulphate is colourless, crystalline solid, M. Pt.  $48^\circ\text{C}$ . It is freely soluble in water. It contains five molecules of water of crystallization which are completely lost at  $215^\circ\text{C}$ .

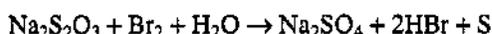
(i) **Action of heat** : On heating above  $220^\circ\text{C}$ , sodium thiosulphate decomposes to give sodium sulphate and sodium penta sulphide.



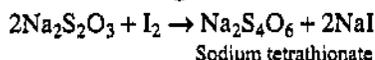
(ii) **Action of dil. acids** : With dil. acids, sodium thiosulphate gives  $\text{SO}_2$  gas and sulphur is precipitated.



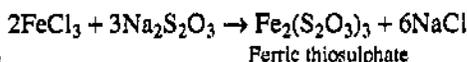
(iii) **Action with halogens** : Sodium thiosulphate is oxidized by chlorine or bromine water into sodium sulphate.



But with iodine, it is oxidized to give sodium tetrathionate.



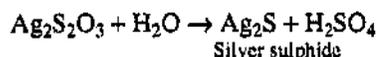
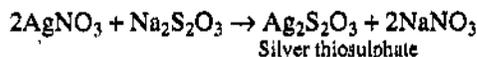
(iv) **Action with  $\text{FeCl}_3$**  : With  $\text{FeCl}_3$  solution, a purple colouration is first produced due to the formation of ferric thiosulphate.



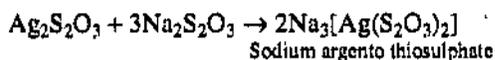
The purple colour disappears shortly afterwards due to its reduction by sodium thiosulphate. The overall reaction is,



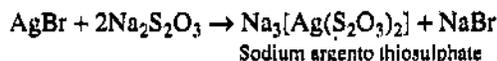
(v) **Action with  $\text{AgNO}_3$**  : With dil. solution of  $\text{Na}_2\text{S}_2\text{O}_3$ , a white ppt. of silver thiosulphate is first formed which changes to yellow, brown and finally black due to the formation of silver sulphide.



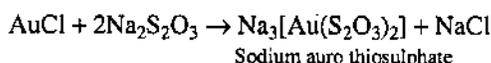
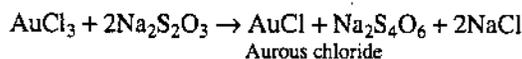
But with conc. solution of  $\text{Na}_2\text{S}_2\text{O}_3$ , the white precipitate of silver thiosulphate first formed, immediately dissolves in an excess of  $\text{Na}_2\text{S}_2\text{O}_3$  to form a soluble complex, sodium argento thiosulphate.



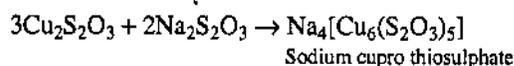
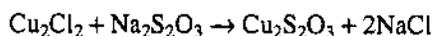
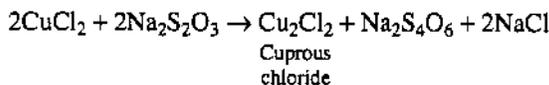
(vi) **Action with silver halides** : Silver halides dissolve in  $\text{Na}_2\text{S}_2\text{O}_3$  to form colourless soluble complex, sodium argento thiosulphate.



(vii) **Action with auric salts** : The auric salts are first reduced to aurous state which then dissolve in an excess of  $\text{Na}_2\text{S}_2\text{O}_3$  to form soluble complex, sodium auro thiosulphate.



(viii) **Action with cupric salts** : The cupric salts are first reduced to cuprous state which then dissolve in an excess of  $\text{Na}_2\text{S}_2\text{O}_3$  to form soluble complex, sodium cupro thiosulphate.



### [III] Uses

Sodium thiosulphate is used :

- (i) As a fixer in photography, *i.e.*, to dissolve the unchanged silver halide.
- (ii) As an antichlor, *i.e.*, to remove last traces of chlorine from the bleached fabric.
- (iii) As a volumetric reagent in the iodometric and iodimetric titrations.
- (iv) For the extraction of silver and gold from their ores.

### • 3.14. PERIODIC DISCUSSION OF VII A GROUP

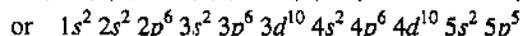
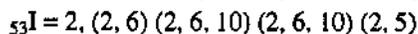
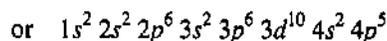
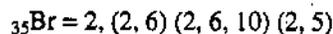
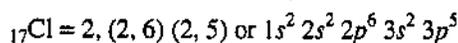
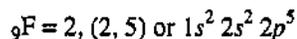
The element fluorine (F), chlorine (Cl), bromine (Br) and iodine (I) are present in the VII A group of the periodic table having atomic numbers 9, 17, 35 and 53, respectively. These elements are collectively known as halogens. The name halogen is derived from the Greek words: halos = sea salts, genes = born, because the salts of chlorine, bromine and iodine are found in the sea water. These are *p*-block elements having the configuration  $ns^2 np^5$  of the outermost shell. Being the elements of the same group, they show many similar properties with regular gradation in their properties. However, fluorine, the first element of the group, differs from rest of the elements of the group because of the following facts :

- (i) Smaller atomic size.
- (ii) Higher electronegativity.
- (iii) Non-availability of empty *d*-orbitals in its valency shell.

The position of these elements in the periodic table is justified due to the following facts :

#### Similarity In Physical Properties

(i) **Electronic configuration** : They all have similar electronic configuration having  $ns^2 np^5$  electrons in the outermost shell.



(ii) **Valency** : The halogens are all mono-valent. This is because they all have one electron less than the stable configuration of a noble gas. In most of their compounds, the halogens complete their octet either by gaining one electron to form mono-negative halide ion ( $\text{X}^-$ ) or by sharing one electron to form a single covalent bond.

(iii) **Non-metallic character** : They are all non-metals.

(iv) **Melting and boiling points** : They have low melting and boiling points.

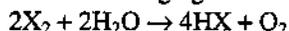
(v) **Atomicity** : They are all diatomic in the gaseous state.

(vi) **Combination with hydrogen** : They all combine with hydrogen to give gaseous hydrides. These hydrides give strongly acidic solutions when dissolved in water.



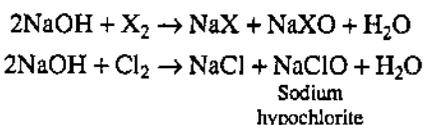
(vii) **Combination with metals and non-metals :** The halogens combine with most of the metals and non-metals to form halides.

(viii) **Action with water :** They decompose water giving oxygen. Iodine, however, reacts with water only in the presence of a reducing agent.

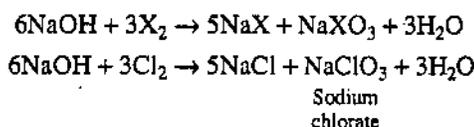


(ix) **Action with alkalis :** Except fluorine, all the halogens react with cold and dilute alkalis to give hypo-halites and with hot and conc. alkalis to give higher oxy salts, halates.

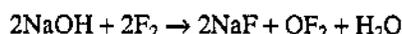
**With cold and dil. alkali :**



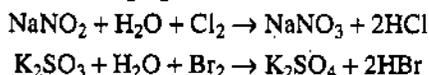
**With hot and conc. alkali :**



Fluorine, however, gives oxygen di-fluoride with alkalis.

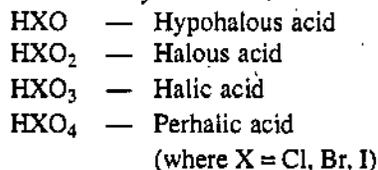


(x) **Oxidizing properties :** Except fluorine, which is very reactive, other halogens in their aqueous solutions act as oxidizing agents. Thus,



(xi) **Formation of interhalogen compounds :** The halogens react with each other to form compounds known as interhalogens. These compounds are of the type AX (ClF, BrF, BrCl, ICl, IBr); AX<sub>3</sub> (ClF<sub>3</sub>, BrF<sub>3</sub>, ICl<sub>3</sub>); AX<sub>5</sub> (BrF<sub>5</sub>, IF<sub>5</sub>) and AX<sub>7</sub> (IF<sub>7</sub>).

(xii) **Formation of oxy acids :** Except fluorine, which does not form any oxy acid, the other halogens form four series of oxyacids.



### Gradation in Properties

(i) Atomic weight, atomic volume, specific gravity, melting and boiling points increase whereas electronegativity and ionization potential decrease as the atomic number increases.

(ii) Fluorine and chlorine are gases, bromine is a liquid, whereas iodine is a solid. Thus, the physical state changes from gas to liquid and then to solid.

(iii) The colour of the vapours becomes denser and denser down the group. Thus, fluorine is pale yellow, chlorine is greenish yellow, bromine is reddish brown and iodine is dark violet.

(iv) Chemical reactivity decreases as we move down the group. This is indicated from the following :

(a) Fluorine reacts with hydrogen in dark and at a low temperature, chlorine reacts in the presence of ultraviolet light, bromine reacts on heating, whereas iodine reacts on heating in the presence of a catalyst.

(b) Fluorine reacts violently with water, chlorine reacts slowly, bromine reacts very slowly, iodine does not react with water.

(c) Fluorine can displace all the halogens from the solutions of their salts, chlorine displaces only bromine and iodine, bromine displaces iodine only and iodine cannot displace any of the halogens.

### • 3.15. ABNORMAL BEHAVIOUR OF FLUORINE

Fluorine, the first element of the group differs from rest of the elements of the group because of the following facts :

(i) Smaller atomic size.

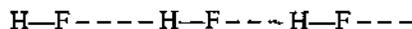
(ii) Higher electronegativity.

(iii) Non-availability of empty *d*-orbitals in its valency shell.

The main points of difference are :

(i) Fluorine exhibits an oxidation state -1 only, whereas remaining halogens may exhibit oxidation state -1, 1, +3, +5 and +7. The higher oxidation states arise due to the presence of vacant *d*-orbitals in their valency shells.

(ii) On account of high electronegativity, fluorine enters into hydrogen bond formation in its compounds with hydrogen. Thus, hydrogen fluoride is an associated molecule due to hydrogen bonding.

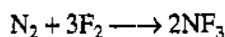
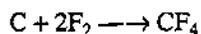


(iii) **Reactivity** : Fluorine is most reactive among the halogens. This is due to high electronegativity, small size of its atom, extremely high oxidizing power and its low F—F bond energy (38.5 k.cals/mole). This is indicated by the following properties :

(a) **Combination with hydrogen** : Fluorine reacts with hydrogen in dark at a low temperature. The other halogens do not react with hydrogen in dark.

(b) **Action with metals** : Fluorine reacts with metals like gold and platinum. The other halogens do not react with these metals.

(c) **Action with non-metals** : Fluorine combines directly with the non-metals like carbon, silicon, nitrogen etc. to form their fluorides.



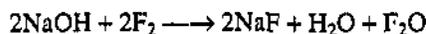
The other halogens do not combine directly with these elements.

(iv) **Action with water** : Fluorine reacts with water giving HF, O<sub>2</sub> and O<sub>3</sub>.



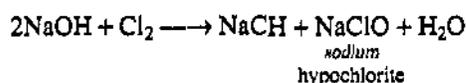
The other halogens do not give ozone with water.

(v) **Action with alkaline** : Fluorine reacts with caustic alkalies to form oxygen difluoride.

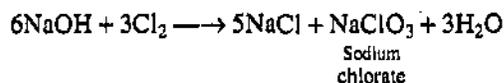


The other halogens react with cold and dilute alkalies to form hypohalites and with hot and conc. alkalies to form higher oxy salts, halates.

**With cold and dilute alkali :**



**With hot and conc. alkali :**



(vi) **Formation of oxy acids** : Fluorine does not form any oxy acid because it is the strongest oxidising agent. The remaining halogens form four types of oxy acids :

HXO - Hypohalous acid

HXO<sub>2</sub> - Halous acid

### • 3.16. INTERHALOGEN COMPOUNDS

*Covalent compounds formed by the combination of two different halogens are known as interhalogen compounds. These compounds are named as halides of less electronegative halogens. Thus, I—Cl is named as iodine monochloride. These compounds contain an atom A of large halogen atom which is bound to an odd number of smaller halogen atoms X and form compounds of the type AX (ClF, BrF, BrCl, ICl, IBr), AX<sub>3</sub> (ClF<sub>3</sub>, BrF<sub>3</sub>, ICl<sub>3</sub>), AX<sub>5</sub> (BrF<sub>5</sub>, IF<sub>5</sub>) and AX<sub>7</sub> (IF<sub>7</sub>) corresponding to the oxidation states +1, +3, +5 and +7 of large halogen atom. Since interhalogen compounds contain odd number of smaller halogen atoms, they are diamagnetic having all the valency electrons present, either as shared or unshared electrons.*

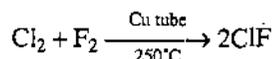
It is observed that as the ratio of radii of A and X increases, the number of atoms per molecule increases. The value of F for Cl is 3, while for Br it is 5 and that for I it is 7. There are never more than two different halogen atoms in any interhalogen compound because such a compound will be unstable.

**Reactivity more than halogens :** Interhalogen compounds are generally more reactive than halogens except  $F_2$ . This is because A—X bond in these compounds is weaker than X—X or A—A bond in halogens.

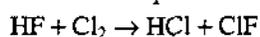
In AX type of compounds, one atom of each halogen is present. The well known compounds of this type are chlorine monofluoride (ClF), bromine monofluoride (BrF), bromine monochloride (BrCl), iodine monochloride (ICl) and iodine monobromide (IBr) etc.

### [I] Chlorine Monofluoride (ClF)

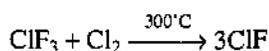
**Preparation :** (i) By direct combination of  $Cl_2$  and  $F_2$ .



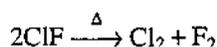
(ii) By the reaction of  $Cl_2$  with HF at liquid air temperature.



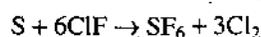
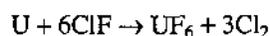
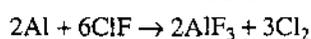
(iii) By heating  $ClF_3$  and  $Cl_2$  in equimolar quantities at  $300^\circ C$ .



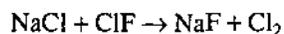
**Properties :** (i) Chlorine monofluoride is a colourless gas having characteristic odour. It dissociates on heating as



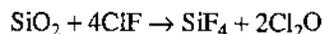
(ii) Chlorine monofluoride reacts with metals and non-metals to form fluorides.



(iii) Chlorine monofluoride reacts with NaCl to form NaF and  $Cl_2$ .

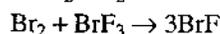
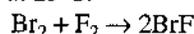


(iv) Chlorine monofluoride reacts with silica to form  $SiF_4$ .



### [II] Bromine Monofluoride (BrF)

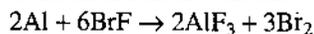
**Preparation :** Bromine monofluoride is prepared by direct combination of  $Br_2$  and  $F_2$  or by the action of  $BrF_3$  on  $Br_2$  at  $25^\circ C$ .



**Properties :** (i) Bromine monofluoride is a reddish brown gas, M. Pt.  $-33^\circ C$ , B. Pt.  $23^\circ C$ . It is unstable and decomposes as :

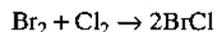


(ii) Bromine monofluoride reacts with metals to form fluorides.

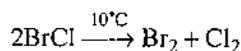


### [III] Bromine Monochloride (BrCl)

**Preparation :** Bromine monochloride is prepared by passing  $Cl_2$  into liquid  $Br_2$  below  $10^\circ C$ .

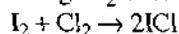


**Properties :** Bromine monochloride is reddish brown liquid, insoluble in water,  $CS_2$  and ether. It dissociates into  $Br_2$  and  $Cl_2$  at  $10^\circ C$ .

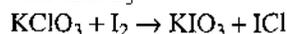


### [IV] Iodine Monochloride (ICl)

**Preparation :** (i) By passing  $Cl_2$  over solid  $I_2$  below  $0^\circ C$ .



(ii) By heating  $I_2$  with  $KClO_3$ .

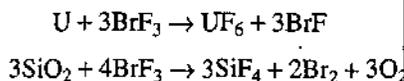


Potassium  
iodate



**Properties.** (i) Bromine trifluoride is a straw coloured liquid, B. Pt.  $127^{\circ}\text{C}$  and M. Pt.  $8.8^{\circ}\text{C}$ .

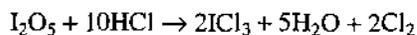
(ii) Bromine trifluoride also acts as a fluorinating agent and reacts with metals, metal oxides to form fluorides.



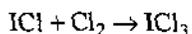
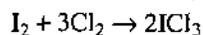
**Uses.** Bromine trifluoride is used as a fluorinating agent.

### [VIII] Iodine Trichloride ( $\text{ICl}_3$ )

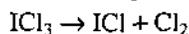
**Preparation :** (i) By heating  $\text{I}_2\text{O}_5$  with HCl acid.



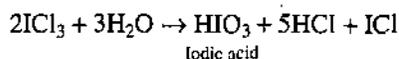
(ii) By the action of excess of  $\text{Cl}_2$  on  $\text{I}_2$  or iodine monochloride at  $100^{\circ}\text{C}$ .



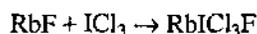
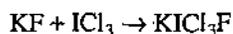
**Properties :** (i) Iodine trichloride is a lemon yellow crystalline solid, M. Pt.  $101^{\circ}\text{C}$ . It has pungent smell. It is unstable and decomposes into  $\text{ICl}$  and  $\text{Cl}_2$  on heating.



(ii) Iodine trichloride is readily hydrolysed by water as :



(iii) Iodine trichloride reacts with fluorides of potassium, rubidium and caesium to form polyhalides.



**Uses :** Iodine trichloride is used in medicines and in the preparation of polyhalides.

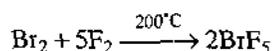
In  $\text{AX}_5$  type of compounds, one atom of large halogen atom combines with five atoms of smaller halogen atoms. The well known compounds of this type are bromine pentafluoride ( $\text{BrF}_5$ ) and iodine pentafluoride ( $\text{IF}_5$ ).

### [IX] Bromine Pentafluoride ( $\text{BrF}_5$ )

**Preparation :** (i) By passing  $\text{F}_2$  into  $\text{BrF}_3$  at  $100^{\circ}\text{C}$  and heating the mixture at  $200^{\circ}\text{C}$ .

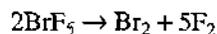


(ii) By the action of excess fluorine diluted with  $\text{N}_2$  on  $\text{Br}_2$  vapour in a copper tube at  $200^{\circ}\text{C}$ .

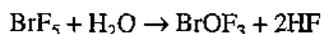


**Properties :** (i) Bromine pentafluoride is a colourless fuming liquid, B. Pt.  $40.5^{\circ}\text{C}$ , M. Pt.  $-61.3^{\circ}\text{C}$ .

(ii) On heating at  $400-500^{\circ}\text{C}$ , bromine pentafluoride dissociates into elements.

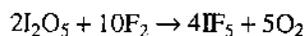
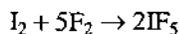


(iii) Bromine pentafluoride violently reacts with water to give HF.

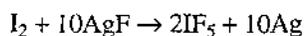


### [X] Iodine Pentafluoride ( $\text{IF}_5$ )

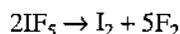
**Preparation :** (i) By passing excess of  $\text{F}_2$  diluted with  $\text{N}_2$  over iodine or iodine pentoxide.



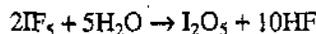
(ii) By heating  $\text{I}_2$  with  $\text{AgF}$ .



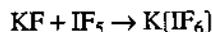
**Properties :** (i) Iodine pentafluoride is a colourless liquid, B. Pt.  $104.5^{\circ}\text{C}$ . It dissociates on heating.



(ii) Iodine pentafluoride reacts rapidly with water to form  $I_2O_5$  and HF.



(iii) Iodine pentafluoride forms complex compounds with alkali metal halides.



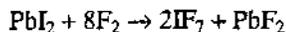
In  $AX_7$  type of compounds, one atom of large halogen combines with seven atoms of small halogen atoms. The only compound of this type is iodine heptafluoride,  $IF_7$ .

### [XI] Iodine Heptafluoride ( $IF_7$ )

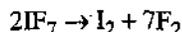
**Preparation :** (i) By heating iodine pentafluoride with  $F_2$  at  $250-300^\circ C$ .



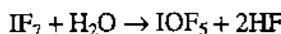
(ii) By the action of excess of  $F_2$  on  $PbI_2$ .



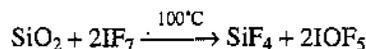
**Properties :** (i) Iodine heptafluoride is a colourless highly reactive gas. It dissociates on heating.



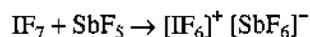
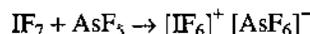
(ii) Iodine heptafluoride is hydrolysed by water to give iodine oxy fluoride and HF.



(iii) Iodine heptafluoride reacts with silica and glass.



(iv) Iodine heptafluoride forms addition compounds with  $AsF_3$  and  $SbF_5$ .

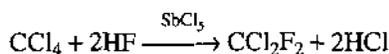
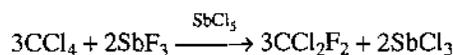


### • 3.17. FREON

The chlorofluoro derivatives of methane and ethane, *i.e.*,  $CHClF_2$ ,  $CCl_2F_2$ ,  $CF_3CHCl_2$  are called *freons*. The most common freon is dichloro difluoro methane commonly known as freon or freon-12.

#### Preparation

Freon is prepared by heating antimony trifluoride or hydrogen fluoride with  $CCl_4$  in the presence of  $SbCl_5$  as catalyst.



#### Properties and Uses

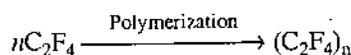
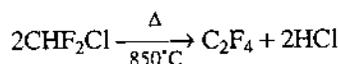
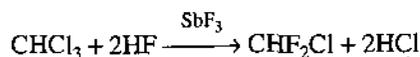
Freon is a colourless, non-toxic and non-inflammable gas, B. Pt.  $-29.6^\circ C$ . It is chemically inert and does not react even with  $O_2$  or  $H_2O$ . It is used in refrigeration and air-conditioning in place of  $NH_3$  and  $SO_2$ .

### • 3.18. TEFLON

Teflon is a polymer of tetrafluoro ethylene.

#### Preparation

Teflon is prepared by the action of HF on  $CHCl_3$  in the presence of  $SbF_3$ .





## • SUMMARY

- Metals like Li, Na, K, Rb, Cs and Fr are called **alkali metals** and belong to IA group of the periodic table. They have one electron in the outermost shell.
- Lithium and magnesium are diagonally related elements.
- Metals like Be, Mg, Ca, Sr, Ba, Ra are called **alkaline earth metals** and belong to II A group of the periodic table. They have two electrons in the outermost shell.
- Beryllium the first element of II A group differs from the rest of elements of its own group, because of its small atomic size and comparatively high electronegativity.
- Metals like B, Al, Ga, In and Tl belong to III A group of the periodic table. They have three electrons in the outermost shell.
- Boranes are compounds of boron and hydrogen and have the general formula  $B_nH_{n+4}$ .
- Metals like C, Si, Ge, Sn and Pb belong to IV A group of the periodic table (Four electrons in the outermost shell).
- Metals like N, P, As, Sb and Bi belong to V A group of the periodic table (Five electrons in the outermost shell).
- Metals like O, S, Se, Te and Po belong to VI A group of the periodic table (Six electrons in outermost shell).
- Elements F, Cl, Br and I are called halogens and belong to VII A group of the periodic table (Seven electrons in outermost shell).
- Covalent compounds formed by the combination of two different halogens are called interhalogen compounds, e.g., ClF, BrF etc.
- **Freon** : The chlorofluoro derivatives of methane and ethane are called freons, e.g.,  $CCl_2F_2$ .
- **Teflon** : It is a polymer of tetrafluoro ethylene, e.g.,  $(C_2F_4)_n$ .

## • TEST YOURSELF

Answer the following questions :

1. Discuss the position of alkali metals in the periodic table with reference to electronic configuration and oxidation state.
2. Discuss the anomalous behaviour of beryllium in the periodic table.
3. Discuss the position of boron in the periodic table.
4. Explain the position of halogens in the periodic table.
5. What are interhalogen compounds ? Mention their preparation and properties.
6. Explain why interhalogen compounds are more reactive than halogens ?
7. Write short notes on the following :  
(i) Freon                      (ii) Teflon
8. Describe the preparation and properties of the following compounds :  
(i) Lithium aluminium hydride      (ii) Diborane      (iii) Sodium thiosulphate      (iv) Borax
9. Beryllium shows diagonal relationship with :  
(a) Mg                      (b) B                      (c) C                      (d) Al
10. Which of the following is the strongest base ?  
(a) LiOH                      (b) NaOH                      (c) KOH                      (d) CsOH
11. Sodium thiosulphate is used in photography because of its :  
(a) Reaction with light                      (b) Reducing behaviour  
(c) Oxidising behaviour                      (d) Complexation behaviour
12. Fill in the blanks :  
(i) Boron resembles more with ..... than its own family members.  
(ii) The halogen with highest electron affinity is .....  
(iii) Teflon is a polymer of .....  
(iv) ..... is the commercial name of sodium thiosulphate.

## ANSWERS

9. (d) 10. (d) 11. (d) 12. (i) silicon (ii) chlorine (iii) tetrafluoro ethylene (iv) hypo



# 4

## NOBLE GASES

### STRUCTURE

- Position of Noble Gases in the Periodic Table
- History of Discovery of Noble Gases
- Isolation of Noble Gases
- Compounds of Noble Gases
- Uses of Noble Gases
  - Student Activity
  - Summary
  - Test Yourself

### LEARNING OBJECTIVES

After going this unit you will learn :

- Discovery of argon, helium and other inert gasses like neon, krypton, xenon and radon.
- Rayleigh and Ramsay methods.
- Dewar's Coconut charcoal method.
- Fractionation of liquid air.
- Different methods to separate the noble gases.
- Compounds and uses of noble gases.

### 4.1. POSITION OF NOBLE GASES IN THE PERIODIC TABLE

The elements helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) belong to zero group of the periodic table. They are also known as rare gases or inert gases, as they form a few compounds under special conditions. The zero group has been inserted between highly electronegative halogens (VII A) and highly electropositive alkali metals (I A).

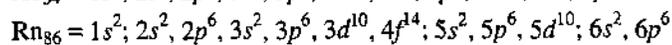
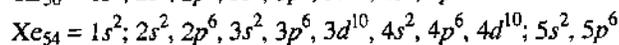
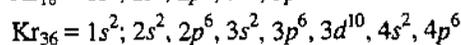
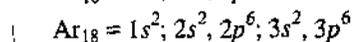
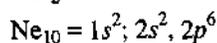
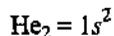
Group VII A	-	F <sub>9</sub>	Cl <sub>17</sub>	Br <sub>35</sub>	I <sub>53</sub>	At <sub>85</sub>	Strongly electronegative
Group 0	He <sub>2</sub>	Ne <sub>10</sub>	Ar <sub>18</sub>	Kr <sub>36</sub>	Xe <sub>54</sub>	Rn <sub>86</sub>	(Inert)
Group I A	Li <sub>2</sub>	Na <sub>11</sub>	K <sub>19</sub>	Rb <sub>37</sub>	Cs <sub>55</sub>	Fr <sub>87</sub>	Strongly electropositive

PERIODS — Horizontal Rows

d-Block Elements or Transition Elements

### Electronic Configuration of Noble Gases

The electronic configuration of all noble gases is shown below :



All these elements have  $ns^2, p^6$  structure of their outermost shell (excepting He, which possesses only one complete shell, i.e.,  $1s^2$ ). Thus, all these gases have a stable outermost shell and their inclusion in the same group of the periodic table is justified.

This position is justified by the following facts :

- (i) Noble gases are chemically inert (zero valent), colourless, odourless and tasteless gases.
- (ii) The ratio  $C^p/C_v$  is the same, i.e., 1.66 for all these elements, which shows their monoatomic nature.
- (iii) Noble gases show a regular gradation in their physical properties. Density, b.p., m.p., etc., increase with rise of atomic numbers.
- (iv) Noble gases form a transition group between highly electronegative halogens and highly electropositive alkali metals.

The above facts justify their position in the periodic table.

## • 4.2. HISTORY OF DISCOVERY OF NOBLE GASES

**Discovery of argon :** Cavendish (1785) subjected air mixed with an excess of oxygen for the continued action of electric sparks and absorbed the resulting oxide of nitrogen and oxygen in potassium pentasulphide (liver of sulphur). He observed that whole of the gas was absorbed except a very small fraction, which was left in the form of a bubble. He repeated the experiment several times and always found a residual gas in the form of a small bubble. He did not, however, draw any conclusion about the nature of this gas and the experiment was forgotten for over a century.

The importance of the experiment was realised after 109 years by Rayleigh (1894) who was trying to study the properties of nitrogen obtained from two different sources. He obtained nitrogen from the atmospheric air and by chemical means. He observed that the density of nitrogen obtained from atmospheric air was 0.5% more than the density of the gas obtained from ammonium nitrite. This showed the presence of a heavier constituent in the atmospheric nitrogen. This made Rayleigh and Ramsay to repeat the forgotten experiment of Cavendish. The residual gas so obtained was now spectroscopically examined. The spectrum of residual gas did not coincide with nitrogen and indicated the presence of a new element. Ramsay (1895) collected the residual gas in sufficient quantity and determined its vapour density which came out to be 20. Its atomic weight was found to be 40. The new gas was named **argon** (from the Greek word *argon* meaning "lazy") due to its inert nature.

**Discovery of helium :** In 1868, Frankland and Lockyer during total solar eclipse in India, spectroscopically examined the chromosphere of the sun and noticed the presence of a new yellow line which did not coincide with  $D_1$  and  $D_2$  lines of sodium. Jansen named it as  $D_3$ . Frankland and Lockyer concluded that it corresponded to an element not present on earth and named it as **helium** (*helios = sun*).

Ramsay showed its existence on earth. In fact, Ramsay was in search of some new source of argon. Miers suggested that Ramsay might investigate mineral cleveite for argon. Ramsay and Travers heated cleveite with dil.  $\text{H}_2\text{SO}_4$  in vacuum and collected the evolved gas. This gas was sent to Crookes for spectrum analysis. The spectrum contained the  $D_3$  line observed by Frankland and Lockyer. Thus, the presence of helium on earth was established.

**Discovery of other inert gases :** Ramsay and Travers obtained the other gases of this group by fractional distillation of argon obtained from atmospheric air. These gases were named as **neon** (new) **krypton** (hidden) and **xenon** (stranger). **Radon** or **nitron** was discovered by Dorn (1900) as disintegration product of radium.

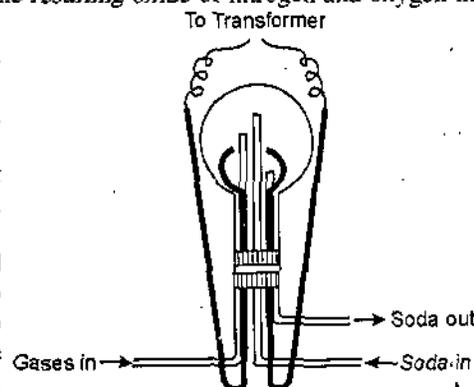
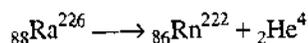


Fig. 1. Rayleigh's experiment

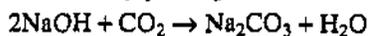
### • 4.3. ISOLATION OF NOBLE GASES

There are two methods for the isolation of noble gases from the atmosphere, viz., chemical methods and fractionation of liquid air.

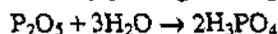
**(1) Chemical methods :** In these methods, first of all, noble gas mixture is isolated from air and then the individual members are separated from this mixture. This is done by any of the following methods.

**(a) Rayleigh and Ramsay first method :** In this method, the different constituents of air, i.e., carbon dioxide, water vapour, oxygen and nitrogen are removed, one by one, as follows :

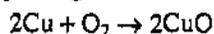
(a) *Carbon dioxide :* By passing over sodalime.



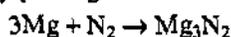
(b) *Water vapour :* By passing over  $\text{P}_2\text{O}_5$ .



(c) *Oxygen :* By passing over red hot Copper.



(d) *Nitrogen :* By passing over heated magnesium.



The process of passing air successively over red hot copper and heated magnesium was repeated till it was completely free from oxygen and nitrogen. The residual gas was found to be mixture of noble gases.

**(b) Rayleigh and Ramsay second method :** In this method, 9 volumes of air and 11 volumes of oxygen are introduced into a glass globe of 50 litre capacity. This glass globe is fitted with two heavy platinum electrodes through which a transformer discharge of 6000-8000 volts is passed. Nitrogen of the air combines with excess of oxygen to form oxides of nitrogen. Now, a continuous stream of caustic soda solution is introduced into the glass globe through a tube. The oxides of nitrogen are absorbed by the alkali and used up caustic soda solution is taken away by another tube.

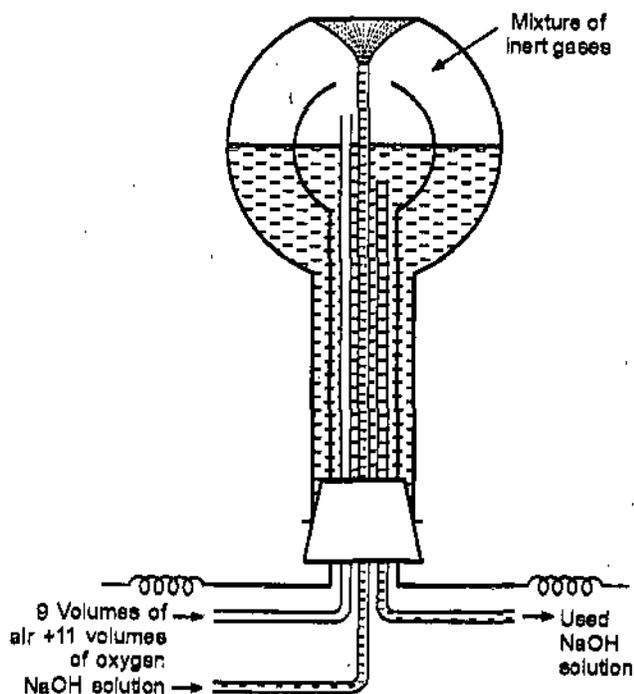
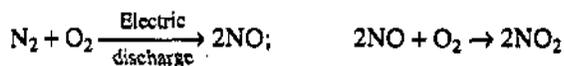


Fig. 2. Rayleigh and Ramsay method for the isolation of noble gases.



The excess oxygen from the remaining gaseous mixture is absorbed by potassium pentasulphide or alkaline pyrogallol solution introduced similarly. The residual gas is found to be a mixture of noble gases.

#### Separation of Noble Gases From Noble Gas Mixture : (Dewar's Coconut Charcoal Method)

This method is based on the fact that coconut charcoal adsorbs different inert gases at different temperatures and, therefore, the separation of these gases may be done. The mixture of noble gases is passed over coconut charcoal which is contained in a double walled bulb and is cooled by liquid air bath at the desired temperatures.

The following flow sheet will illustrate the method.

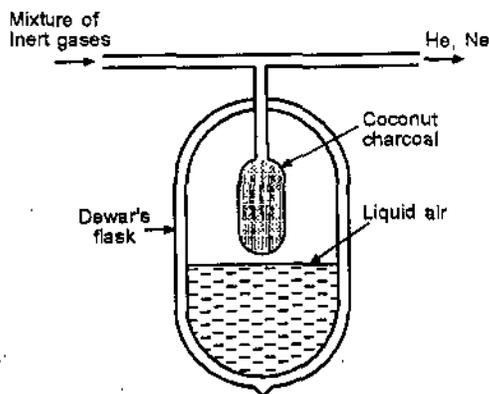
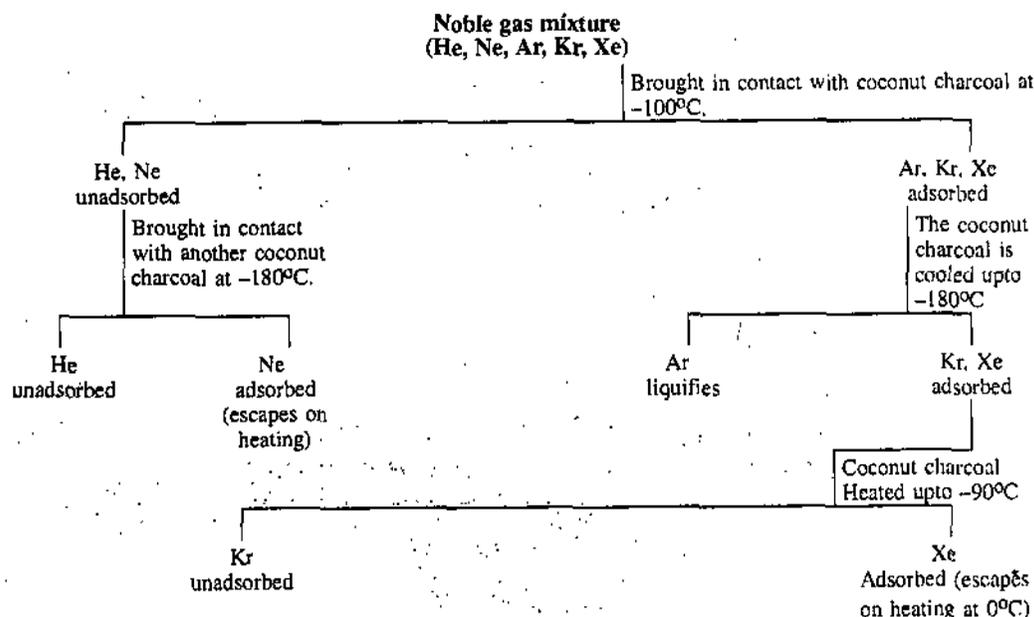
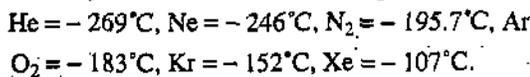


Fig. 3. Separation of noble gases by Dewars' coconut charcoal method.



**(2) Fractionation of liquid air :** The noble gases may be separated by fractional evaporation of liquid air. The method is based on the fact that the boiling points of various constituents of liquid air widely differ from each other, e.g.,



The apparatus consists of two fractionating columns constructed one above the other. These columns are provided with baffle plates on the inner side and there is a reservoir containing liquid oxygen in between these columns. Cooled and compressed air is introduced into the column. The cooling is caused due to expansion (Joule-Thomson effect) resulting in liquefaction of less volatile fraction containing oxygen, argon, krypton, xenon and a little of nitrogen (fraction A). The remaining gases helium, neon and nitrogen rise upwards in the column, where they are cooled and are also liquified (fraction B).

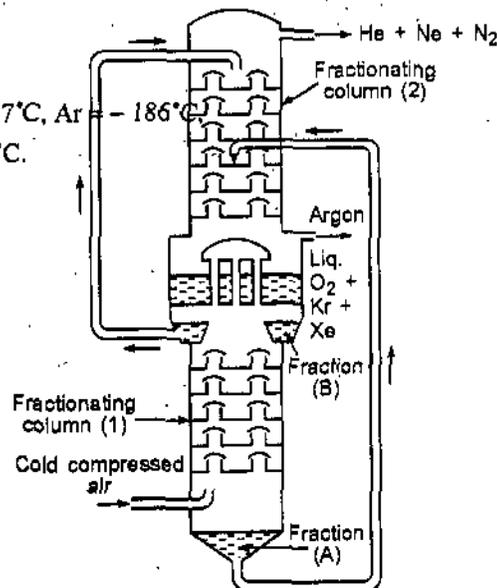


Fig. 4. Fractionation of liquid air.

The fraction A is pumped up from the bottom and is dropped from the middle of the upper fractionating column. The fraction B is also pumped and is dropped from the top of the upper fractionating column. From this the liquid air is separated into three fractions as follows :

- (i) The first fraction contains most volatile gases helium, neon and nitrogen. These gases escape from the top of the fractionating column.
- (ii) The second fraction contains argon and oxygen. These gases escape from the top of central reservoir.
- (iii) The third fraction contains liquid oxygen, krypton and xenon. These are collected at the bottom of the reservoir.

From these fractions, the noble gases are obtained separately as follows:

(a) **Separation of helium and neon** : The first fraction containing He, Ne and N<sub>2</sub> is passed through a spiral tube cooled by liquid nitrogen. Here most of the nitrogen is condensed and a mixture of He, Ne and some N<sub>2</sub> passes out. The remaining N<sub>2</sub> is removed by passing the mixture over heated calcium carbide.

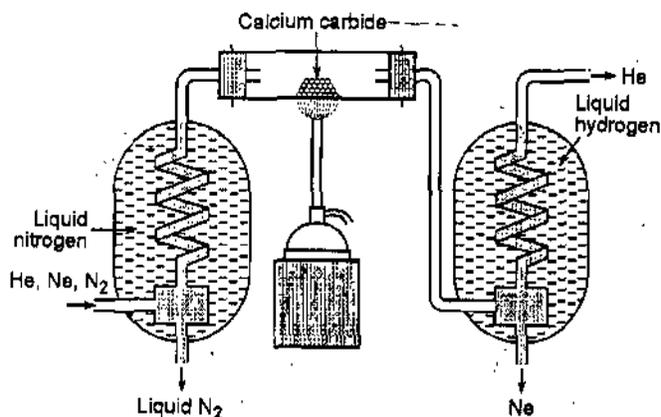
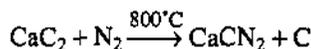
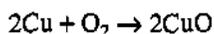


Fig. 5. Separation of He and Ne.



The gaseous mixture containing He and Ne is then passed through a spiral tube cooled by liquid H<sub>2</sub> at -253°C, when Ne solidifies (B. Pt. -246°C) and is collected at the bottom, while helium in the gaseous state escapes from the top.

(b) **Separation of argon** : The second fraction containing argon and oxygen is passed through a column which is provided with a coil in which liquid N<sub>2</sub> is being circulated. Here most of the oxygen is condensed, while more of argon escapes at the top. The argon, so obtained, still contains some oxygen which is removed by passing over heated copper.



(c) **Separation of krypton and xenon** : From the third fraction containing liquid O<sub>2</sub>, Kr and Xe, oxygen is removed by evaporation. The remaining liquid becomes richer in krypton and xenon. These two gases may be separated easily by fractional evaporation as there is a wide difference in their boiling points (Kr = -152°C, Xe = -107°C).

#### • 4.4. COMPOUNDS OF INERT GASES

The atoms of inert gases have completed shells and, therefore, they are chemically inert. Recent researches have shown that under certain specified conditions, they enter into chemical combinations, and form some rare chemical compounds. The specified conditions and types of compounds formed are as follows :

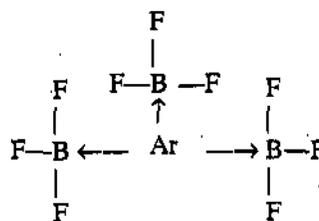
##### [I] Compounds Formed Under Excited Conditions

These compounds, known as **helides**, are formed by sparking helium at low pressure in presence of mercury, tungsten etc. to form HgHe<sub>2</sub>, HgHe<sub>10</sub>, WHe<sub>2</sub>. In addition, metal electrodes in the discharge tubes also form compounds with helium like BiHe<sub>2</sub>, FeHe, Pt<sub>3</sub>He, PdHe. In these compounds, it is supposed that helium is adsorbed on the surface of the metal and, therefore, these compounds are not considered as true chemical compounds.

##### [II] Compounds Formed Through Coordination

Booth and Wilson (1935) reported that argon forms a number of unstable compounds with

varying numbers of  $\text{BF}_3$  molecules, e.g.,  $\text{Ar}\cdot\text{BF}_3$ ,  $\text{Ar}\cdot 2\text{BF}_3$ ,  $\text{Ar}\cdot 3\text{BF}_3$ ,  $\text{Ar}\cdot 6\text{BF}_3$ ,  $\text{Ar}\cdot 8\text{BF}_3$  and  $\text{Ar}\cdot 16\text{BF}_3$ . In these compounds, argon atom donates a pair of electrons to boron atom. In the case of higher compounds, fluorine atoms also donate pair of electrons as shown below :

(Structure of  $\text{Ar}\cdot 3\text{BF}_3$ )

### [III] Compounds With Water

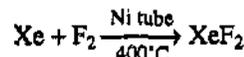
The inert gases argon, krypton and xenon form compounds with water at low temperature and high pressure. These compounds are known as hydrates. The compounds like  $\text{Ar}\cdot 6\text{H}_2\text{O}$ ,  $\text{Kr}\cdot 6\text{H}_2\text{O}$  and  $\text{Xe}\cdot 6\text{H}_2\text{O}$  have been obtained and studied.

### [IV] Compounds Formed by Physical Trapping

The inert gases argon, krypton and xenon form solid compounds with certain organic molecules such as phenol, hydroquinone,  $\text{C}_6\text{H}_4(\text{OH})_2$  under pressure. In these compounds, the inert gases are enclosed into the crystal lattices of the organic molecules. These compounds are known as clathrates. The gas escapes only when the clathrate is dissolved. Helium and neon do not form clathrates due to the small sizes of their atoms which enable them to escape from the lattices of organic molecules.

### Some Compounds of Noble Gases

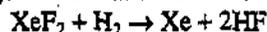
(1) **Xenon difluoride ( $\text{XeF}_2$ )** : It is obtained by heating xenon and fluorine in the ratio of 1 : 3 in a nickel tube at  $400^\circ\text{C}$ .



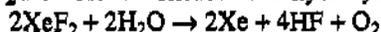
On cooling the vapours, xenon difluoride is obtained as a colourless solid.

**Properties :**  $\text{XeF}_2$  is a colourless solid, M. Pt.  $127^\circ\text{C}$ . It dissolves in liquid hydrogen fluoride.

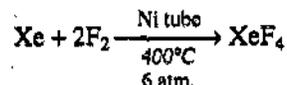
**Action with hydrogen :** Xe and HF are obtained.



**Action with  $\text{H}_2\text{O}$  :** Xenon difluoride is hydrolysed by water to give oxygen.

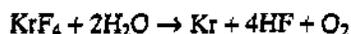
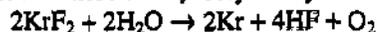


(2) **Xenon tetrafluoride ( $\text{XeF}_4$ )** : It is obtained by heating xenon and fluorine in the ratio of 1 : 5 in a nickel tube at  $400^\circ\text{C}$  and under 6 atmosphere pressure.



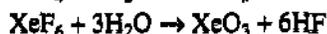
**Properties :**  $\text{XeF}_4$  is a colourless crystalline solid, M. Pt.  $100^\circ\text{C}$ . It is quite stable. It dissolves in liquid hydrogen fluoride.

(3) **Fluorides of krypton :** Recently, it was observed that krypton also combines with  $\text{F}_2$  above  $400^\circ\text{C}$  to form krypton difluoride and krypton tetrafluoride. These fluorides are less stable as compared to xenon fluorides. These are hydrolysed by water according to the equations :



(4) **Radon fluoride ( $\text{RnF}_4$ )** : It has also been prepared similarly as explained above but it is a very unstable compound.

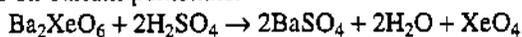
(5) **Xenon trioxide ( $\text{XeO}_3$ )** : Xenon trioxide is obtained in small amounts by the hydrolysis of  $\text{XeF}_4$  or  $\text{XeF}_6$ .



**Properties :** Xenon trioxide is a white solid, soluble in water. Its aq. solution is quite stable but it explodes violently when dry. It produces the same effect as T.N.T. Xenon trioxide dissolves in  $\text{NaOH}$  to form sodium perxenate.



(6) **Xenon tetroxide (XeO<sub>4</sub>)** : Xenon tetroxide is prepared by the action of anhydrous sulphuric acid on barium perxenate.



Xenon tetroxide is less stable than xenon trioxide.

## • 4.5. USES OF NOBLE GASES

### Uses of Helium

(i) Helium is used for filling in balloons and airships as it is a light and non-combustible gas. For this purpose, a mixture of 85% helium and 15% hydrogen is generally used.

(ii) The mixture of helium and oxygen is used for respiration by sea divers. The air proves harmful because nitrogen of the air dissolves in the blood at high pressure when the diver is under deep sea. When he comes to the surface, the pressure is suddenly decreased. The bubbles of nitrogen gas now escape from the blood and get collected at joints which cause pain. Helium, taken in place of air, is much less soluble in blood at high pressure.

(iii) The mixture of helium and oxygen is also used for the artificial breathing of asthma patients. This mixture keeps breathing steady.

(iv) Liquid helium is used for producing low temperatures required for research work.

(v) For producing inert atmosphere in the welding and metallurgy of certain metals which are easily oxidised helium is used.

(vi) Helium is used in the preservation of food.

(vii) Helium nucleus ( $\alpha$ -particle) is used as a bombarding particle for the artificial disintegration of atoms.

### Uses of Neon

(i) Neon gas is used in neon signs used for advertising purposes. The neon lights are visible from long distances and are visible even through fog and mist.

(ii) Neon gas is used in electronic equipments such as voltage stabilizers, current rectifiers.

### Uses of Argon

(i) A mixture of argon with 15% nitrogen is filled in electric bulbs to increase the life of the filament.

(ii) Argon is used for producing inert atmosphere in welding and metallurgy of certain metals which are easily oxidised.

(iii) Argon is used in filling fluorescent tubes and radio-valves.

(iv) Argon is mixed with neon in neon signs to obtain lights of varying colours.

### Uses of Krypton and Xenon

(i) Krypton and xenon are used for filling in electrical bulbs. These gases are superior to argon for this purpose.

(ii) Krypton and xenon are used in discharge tubes for producing high speed flash of bluish light used in quick photography.

### Use of Radon

Radon is used in the treatment of cancer and in radioactive research.



## • SUMMARY

- Helium (He), neon (Ne), argon (Ar), krypton (Kr), Xenon (Xe) and radon (Rn) are called noble gases.
- Noble gases are also known as inert gases, as they form a few compounds under special conditions. They are also called rare gases, as they are found in very small quantities in atmosphere.
- The outermost shell of the inert gases except He is complete with 8 electrons. Helium has only one complete shell with 2 electrons.
- Inert gases are kept in zero group of the periodic table, in between strongly electropositive alkali metals (I-A group) and strongly electronegative halogens (VII-A group).
- Inert gases can be isolated from chemical methods as well as by fractionation of liquid air.
- Helium is used for filling balloons and airships.
- Liquid helium is used for producing low temperatures.
- A mixture of argon with 15%  $N_2$  is filled in electric bulbs to increase the life of the filament.

## • TEST YOURSELF

1. Discuss the position of noble gases in the periodic table.
2. Give a brief history of the discovery of noble gases.
3. How are noble gases isolated from atmosphere?
4. Give a brief account of the compounds of noble gases.
5. Describe the applications of noble gases.
6. The maximum number of compounds are formed by :  
(a) He                      (b) Ne                      (c) Ar                      (d) Xe
7. The inert gas which is substituted by nitrogen in air used by sea divers for breathing is :  
(a) He                      (b) Ne                      (c) Ar                      (d) Rn
8. The noble gas which is not adsorbed by coconut charcoal is :  
(a) He                      (b) Ne                      (c) Ar                      (d) Kr
9. The number of electrons in the outermost shell of helium are :  
(a) 8                      (b) 18                      (c) 32                      (d) 2
10. Fill in the blanks :  
(i) The inert gas with radioactive properties is .....
- (ii) Except helium, the general electronic configuration of zero group elements is .....
- (iii) Noble gases are the end members of each ..... of the periodic table.
- (iv) The electronegativity of zero group element is .....

## ANSWERS

6. (d) 7. (a) 8. (a) 9. (d) 10. (i) radon (ii)  $ns^2np^6$  (iii) period (iv) zero



## RADIOACTIVITY

## STRUCTURE

- Radioactivity
- Theory of Radioactive Disintegration
- Half Life Period
- Average Life Period
- Radioactive Disintegration Series
- Radioactive Equilibrium
- Artificial Disintegration or Transmutation of Atoms
- Artificial Radioactivity
- Nuclear Reactions
- Nuclear Fission (Atomic Fission)
- Nuclear Fusion (Atomic Fusion)
- Applications of Radioactive Isotopes
  - Summary
  - Student Activity
  - Test Yourself

## LEARNING OBJECTIVES

After going this unit you will learn :

- Becquerel rays, radioactive rays and natural radioactivity.
- Properties of  $\alpha$ ,  $\beta$  and  $\gamma$ -rays.
- Group displacement law.
- Thorium, uranium, neptunium and actinium series.
- Bohr's theory of nuclear reactions and classification of nuclear reactions.
- Difference between nuclear fission and nuclear fusion.
- Determination of age of rocks, minerals, archeological specimens and biological specimens.

## • 5.1. RADIOACTIVITY

After the discovery of X-rays by Rontgen in 1895, Henry Becquerel (1896) observed that uranium mineral continuously emits rays which can :

- (i) Affect a photographic plate wrapped in thick layers of black paper. The affected portions became black after the treatment with a developer.
- (ii) Ionise the gases through which they pass.
- (iii) Penetrate through thin sheets of metal foils.
- (iv) Produce fluorescence on striking with zinc sulphide or barium platinocyanide screen.
- (v) Can not be seen by naked eyes.

These active radiations were initially called *Becquerel rays* and later on were called *radioactive rays*. The substances which emit these rays are called *radioactive substances* and the phenomenon is called *natural radioactivity*.

*Natural radioactivity is, thus, a natural spontaneous, continuous disintegration process in which one element decays to give another element.* It is an exothermic process as the energy of the parent element is greater than the energy of products.

Madam Curie and her husband P. Curie in 1902 separated two new radioactive elements, polonium and radium from uranium mineral pitch blende. At the same time, the radioactive elements thorium and actinium were discovered. Thereafter, a number of radioactive elements such as

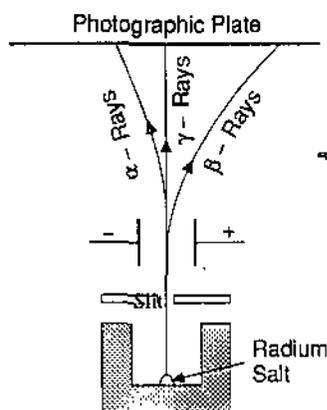


Fig. 1. Deflection of radioactive rays in a magnetic field.

francium (Fr), astatine (At), radon (Rn) were discovered. From the study in the field of radioactivity, it has been found that all the elements after atomic number 83 are radioactive.

### [I] Properties of Radioactive Rays

Rutherford in 1902 observed that these radiations could be divided into three separate beams by passing them between two oppositely charged plates. These beams were called as  $\alpha$ ,  $\beta$ ,  $\gamma$  rays.  $\alpha$ -rays were deflected through a small angle towards the negatively charged plate,  $\beta$ -rays were deflected through a large angle towards the positively charged plate, whereas  $\gamma$ -rays remained unaffected. This indicates that  $\alpha$ -rays are positively charged,  $\beta$ -rays negatively charged, whereas  $\gamma$ -rays are electrically neutral.

#### (1) Properties of $\alpha$ -Rays

(i) **Nature** : These rays consist of positively charged particles called  $\alpha$ -particles. They have two units of positive charge and their mass is four times greater than the mass of hydrogen atom (equal to helium atom). They are, thus, helium nuclei consisting of two protons and two neutrons.

(ii) **Velocity** : They have a velocity of about  $1/10$  of the velocity of light.

(iii) **Kinetic energy** : They have a high kinetic energy due to large mass.

(iv) **Ionization** : They cause ionization of the gases through which they pass. The ionizing power of these rays is greater than that of  $\beta$  or  $\gamma$ -rays.

(v) **Penetrating power** : The penetrating power of these rays is less as they are relatively larger in size. They cannot penetrate through an aluminium foil 0.1 mm thick.

(vi) **Luminescence and photographic activity** : Due to high kinetic energy they can produce luminescence on striking with zinc sulphide or barium platinocyanide screen. They can also affect a photographic plate.

#### (2) Properties of $\beta$ -Rays

(i) **Nature** : These rays consist of negatively charged particles which have the same  $e/m$  ratio as that of electrons. They have charge  $-1$  unit and mass equal to  $1/1838$  of the mass of hydrogen atom. They are, thus, identical with electrons.

(ii) **Velocity** : They have a velocity of about  $9/10$  of the velocity of light.

(iii) **Kinetic energy** : Due to small mass, their kinetic energy is much less than that of  $\alpha$ -particles.

(iv) **Ionization** : They cause little ionization of the gases through which they pass. The ionizing power of these rays is about  $1/100$  of that of  $\alpha$ -rays.

(v) **Penetrating power** : The penetrating power of these rays is more than that of  $\alpha$ -rays. This is due to their small mass and high velocity. They cannot penetrate through an aluminium foil 1 cm thick.

(vi) **Luminescence and photographic activity** : Due to small kinetic energy, they can produce little luminescence on striking zinc sulphide or barium platinocyanide screen. Their photographic activity is, however, greater than that of  $\alpha$ -rays. This is because  $\beta$ -rays, on striking with matter, produce X-rays which have greater photographic activity.

#### (3) Properties of $\gamma$ -Rays

(i) **Nature** : They carry no charge and are non-material. They are high frequency electromagnetic radiations whose wavelength is even less than that of X-rays.

(ii) **Velocity** : They have almost same velocity as that of light.

(iii) **Kinetic energy** : Their kinetic energy is almost zero.

(iv) **Ionization** : They have very little ionizing power, about  $1/100$  of that of  $\beta$ -rays.

(v) **Penetrating power** : Due to their non-material nature and high velocity, they are most penetrating of the three types of radioactive rays. They can penetrate through aluminium foil 1 cm thick.

(vi) **Luminescence and photographic activity** : They produce very little luminescence on striking with zinc sulphide or barium platino-cyanide screen. They affect the photographic plate to a very little extent.

### [II] Unit of Radioactivity

The unit of radioactivity is *Curie* (Ci) or *Rutherford* (Rh), Curie is defined as an activity of any radioactive substance which has a decay rate of  $3.7 \times 10^{10}$  disintegrations per second. This decay rate is based upon the fact that one gram of radium disintegrates at the rate of  $3.7 \times 10^{10}$  disintegrations per second. The smaller units milli-curie and micro-curie are also used.

1 milli curie (m Ci) =  $3.7 \times 10^7$  disintegrations per second

1 micro curie ( $\mu$  Ci) =  $3.7 \times 10^4$  disintegrations per second

The other unit of radioactivity Rutherford is defined as an activity of any radioactive substance which has a decay rate of  $10^6$  disintegrations per second.

### [III] Difference Between Radioactive Changes and Ordinary Chemical Changes

In a radioactive change, there is formation of new substances. It is, therefore, a chemical change. However, this change is different from ordinary chemical change in the following respects—

(1) Radioactivity remains unaffected by physical factors such as pressure, temperature etc. Thus, if a radioactive substance is heated to a high temperature or subjected to vacuum, the amount of radiations will remain the same.

(2) The radioactivity of an element is not affected by other element or elements compounded with it. Thus, one gram of radium in its elementary state or in the form of salts, *i.e.*, radium nitrate or radium bromide will produce the same intensity of radioactivity. This indicates that radioactivity is a property of nucleus and is not concerned with outer electrons.

(3) The energy produced during radioactive changes is million times greater than the energy produced during ordinary chemical changes involving the same weight of the substance.

(4) The nuclear reactions are balanced in terms of both mass and energy, whereas the chemical reactions are balanced in terms of mass only.

(5) In the radioactive change the nucleus of the atom undergoes a change, whereas in the ordinary chemical changes, there is a rearrangement of outer electrons and atomic nuclei remain unaffected.

## • 5.2. THEORY OF RADIOACTIVE DISINTEGRATION

The theory of radioactivity disintegration was given by Rutherford and Soddy in 1903 to explain the phenomenon of radioactivity. According to this theory—

(i) Radioactivity is the property of the nucleus and is thus shown by those elements whose nuclei are unstable.

(ii) The instability of the nucleus is related to neutron ( $n$ ), proton ( $p$ ) ratio, *i.e.*,  $\frac{n}{p}$ . For a given atomic number the stable nuclei have a definite value of  $\frac{n}{p}$  ratio and the nuclei are unstable when this ratio is too high or too low.

When a graph is plotted between the number of neutrons against number of protons for the nuclei of various elements, it has been observed that the stable nuclei lie within the shaded area,

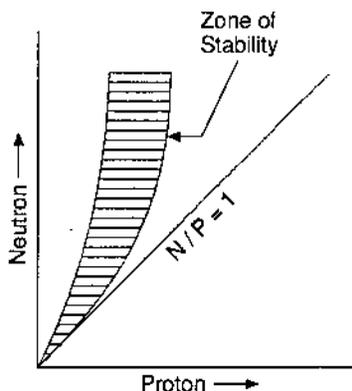
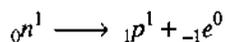


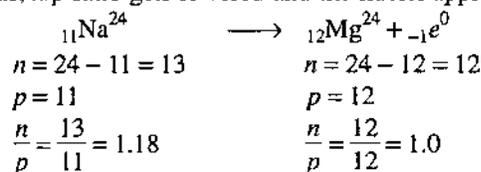
Fig. 2. Graph between number of neutrons against number of protons.

which is known as *zone or region of stability*. The nuclei whose  $n/p$  ratio lies above or below the shaded area, are unstable and undergo spontaneous radioactive disintegration giving  $\alpha$  and  $\beta$  particles. This process continues unless a stable nucleus is produced.

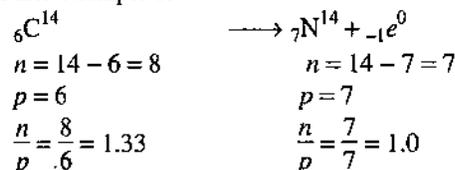
The nuclei lying above the zone of stability have an excess of neutrons. In such a case, there is an emission of  $\beta$ -particles, which correspond to the transformation of neutron to proton.



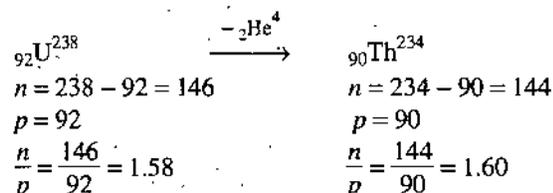
Thus,  $n/p$  ratio gets lowered and the nuclei approach the zone of stability. For example,



Another example is

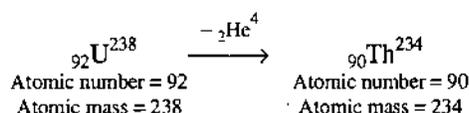


The nuclei lying below the zone of stability, have an excess of protons. In such a case, there is an emission of  $\alpha$ -particles. Thus,  $n/p$  ratio gets increased and the nuclei approach the zone of stability.

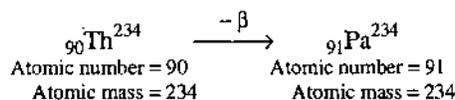


(iii) The nucleus of a radioactive element undergoes spontaneous disintegration and forms nucleus of a new element whose physical and chemical properties are different from those of parent element. The new element may be again radioactive and may emit  $\alpha$  or  $\beta$  particle to form yet another element. A series of changes may occur unless finally a stable element is produced.

(iv) The nature of the new atoms produced depends upon the nature of the particles lost. The loss of  $\alpha$ -particle means that the resulting atom has its atomic number decreased by two units and atomic mass decreased by four units.



Similarly, the loss of  $\beta$ -particle means that the resulting atom has atomic number increased by one unit and there is no change in the atomic mass.



(v) Gamma rays are secondary radiations. After the emission of an  $\alpha$  or  $\beta$  particle, the resulting nucleus becomes excited. After a definite time interval, this excited nucleus changes to a more stable state with the emission of extra energy in the form of  $\gamma$ -rays.

(vi) The rate of radioactive disintegration at any instant is directly proportional to the number of atoms present at that instant *i.e.*,

$$-\frac{dN}{dt} \propto N$$

or

$$-\frac{dN}{dt} = kN$$

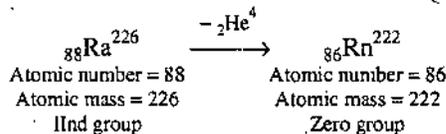
where  $N$  is the number of atoms present in a radioactive substance at any instant and  $dN$  is the number of atoms disintegrated in time  $dt$ .  $k$  is decay constant or disintegration constant or radioactive constant.

(vii) The rate of radioactive disintegration is not affected by physical factors such as pressure, temperature etc.

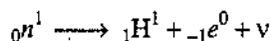
**(1) Group Displacement Law**

The group displacement law was given by Soddy and Fajans in 1913 to show the effect of  $\alpha$  and  $\beta$ -ray changes. According to this law, "in an  $\alpha$ -ray change, the new element occupies a position two places to the left in the periodic table and has atomic mass less by four units than the parent element, whereas in a  $\beta$ -ray change, the new element occupies a position one place to the right in the periodic table and has the same atomic mass as that of the parent element".

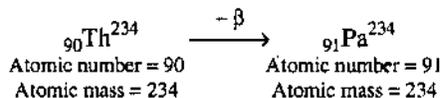
**(i)  $\alpha$ -Ray change :** When an  $\alpha$ -particle ( ${}_2\text{He}^4$ ) leaves the nucleus, it takes away from it the two units of positive charge and four units of mass. Thus, the atomic number of the new element will be decreased by two units and the atomic mass will be decreased by four units. Since, in the modern periodic table, the elements are arranged in order of increasing atomic numbers, therefore, due to the decrease of atomic number by two units, the resulting atom will occupy a position two places to the left in the periodic table from the parent element. For example,



**(ii)  $\beta$ -Ray change :** Similarly, when a  $\beta$ -particle, i.e., electron leaves the nucleus, the resulting atom occupies a position one place to the right in the periodic table. The  $\beta$ -particles are not present in the nucleus and their emission corresponds to the transformation of neutron into proton and neutrino. The neutrino has no rest mass and carries no charge. It only acts as a carrier of energy.

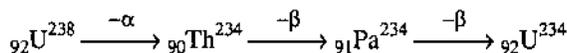


Thus, the number of protons in the nucleus, i.e., atomic number is increased by one unit and, therefore, the resulting atom occupies a position one place to the right in the periodic table.



The emission of  $\gamma$ -rays changes neither the atomic number nor the mass number of the radioactive element and, therefore, does not affect the position of the element in the periodic table.

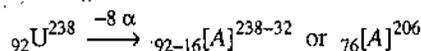
This law is particularly helpful in showing the formation of isotopes and isobars.



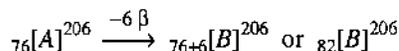
Thus,  ${}_{92}\text{U}^{238}$  and  ${}_{92}\text{U}^{234}$  are isotopes, whereas  ${}_{90}\text{Th}^{234}$ ,  ${}_{91}\text{Pa}^{234}$  and  ${}_{92}\text{U}^{234}$  are isobars. Thus, it is clear that by the loss of one alpha and two  $\beta$ -particles, isotopes are formed, whereas by the loss of  $\beta$ -particle, isobars are formed.

**Ex. 1 :**  ${}_{92}\text{U}^{238}$  emits  $8\alpha$  and  $6\beta$  particles. What would be the atomic number and atomic mass of new atom produced ?

**Solution.** Since by the loss of an  $\alpha$ -particle, the atomic number is decreased by 2 units and atomic mass is decreased by 4 units, therefore, by the loss of  $8\alpha$  particles the atomic number should be decreased by  $8 \times 2 = 16$  units and atomic mass should be decreased by  $8 \times 4 = 32$  units. The change may be represented as—



Now, since by the loss of 1  $\beta$  particle, the atomic number is increased by 1 unit, whereas the atomic mass remains the same, therefore, by the loss of  $6\beta$  particles atomic number should be increased by  $6 \times 1 = 6$  units and there should be no change in the atomic mass. The change may be represented as :



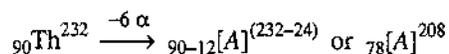
Therefore, the atomic weight of resulting atom is 206 and atomic number is 82.

**Ex. 2 :** The atomic number of thorium is 90 and its atomic mass is 232. How many  $\alpha$ - and  $\beta$ -particles should be emitted so as to obtain a stable isotope of lead? (Atomic number = 82, Atomic weight = 208).

**Solution.** We know that decrease in the atomic mass is due to the loss of  $\alpha$ -particles. In this case, the decrease of atomic mass is  $232 - 208 = 24$  units.

Since 4 units of atomic mass are decreased by the loss of 1  $\alpha$  particle, therefore, 24 units of atomic mass are decreased by the loss of  $24/4 = 6\alpha$  particles.

Thus, by the loss of 6  $\alpha$  particles atomic number is decreased by  $6 \times 2 = 12$  units. The change may be represented as:



Now the final product to be obtained is an isotope of lead having atomic number 82 and atomic mass 208. Since by the loss of 1  $\beta$  particle atomic number is increased by one unit, therefore, to increase the atomic number by four units, there should be a loss of 4  $\beta$  particles. The change may be represented as—

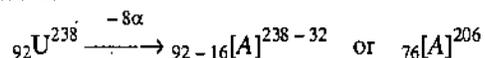


Thus, there should be a loss of 6  $\alpha$  and 4  $\beta$  particles.

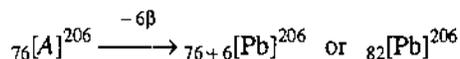
**Ex. 3 :** Uranium (atomic weight 238 and atomic number 92) finally disintegrates to give an isotope of lead (atomic weight 206 and atomic number 82). How many alpha and beta particles will be emitted?

**Solution.** We know that decrease in the atomic mass is due to the loss of  $\alpha$ -particles. In this case, the decrease of atomic mass is  $238 - 206 = 32$  units. Since 4 units of atomic mass are decreased by the loss of 1  $\alpha$  particle, therefore 32 units of atomic mass are decreased by the loss of  $\frac{32}{4} = 8\alpha$ -particles. Thus, by the loss of 8  $\alpha$  particles atomic number is decreased by  $8 \times 2 = 16$  units.

The change may be represented as —



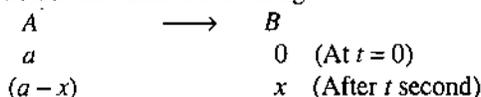
Now, the final product to be obtained is an isotope of lead having atomic number 82 and atomic mass 206. Since by the loss of 1  $\beta$  particle atomic number is increased by one unit, therefore, to increase the atomic number by six units, there should be a loss of 6  $\beta$ -particles. The change may be represented as —



Thus, there should be a loss of 8  $\alpha$  and 6  $\beta$ -particles.

The rate of radioactive decay is directly proportional to the quantity of radioactive substance. Thus, it is clear that the rate of radioactive decay goes on decreasing with time. Thus, the time required for the complete decay of any radioactive substance will be infinite. Therefore, the value taken is the half life period. It is the time required for the decay of one half of the radioactive substance originally taken.

Consider the radioactive change—



Let  $a$  be the initial concentration of A. After  $t$  second  $x$  atoms of  $a$  disintegrate leaving behind  $(a - x)$  atoms. Since the rate of radioactive decay is directly proportional to the quantity of radioactive substance, therefore,

$$\frac{dx}{dt} \propto (a - x)$$

$$\text{or} \quad \frac{dx}{dt} = k(a - x)$$

where  $k$  is known as *decay constant*, *disintegration constant* or *radioactive constant*. It is defined as the *rate of radioactive disintegration when the number of radioactive nuclei present is one*.

$$\text{or} \quad \frac{dx}{(a - x)} = k \cdot dt$$

Integrating, we have

$$-\log_e (a - x) = kt + I \quad \dots (1)$$

where  $I$  is known as integration constant, the value of which depends upon the primary conditions.

When  $t = 0$ ,  $x = 0$ .

$$\therefore -\log_e (a - 0) = k \times 0 + I$$

or

$$-\log_e a = I$$

Putting the value of  $I$  in equation (1),

$$-\log_e (a-x) = kt - \log_e a$$

$$kt = \log_e a - \log_e (a-x)$$

or

$$kt = \log_e \frac{a}{(a-x)}$$

or

$$k = \frac{1}{t} \log_e \frac{a}{(a-x)}$$

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

This is the same equation as obtained for a first order reaction. Hence, radioactive decay is a first order reaction.

### • 5.3. HALF LIFE PERIOD

Half life period is the time required for the decay of one half of the radioactive substance originally taken. We know that—

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

When half of A disintegrates into B, then  $x = a/2$  and  $t = T_{1/2}$  (Half life period)

$$\begin{aligned} \therefore T_{1/2} &= \frac{2.303}{k} \log_{10} \frac{a}{a-a/2} \\ &= \frac{2.303}{k} \log_{10} \frac{a}{a/2} = \frac{2.303}{k} \log_{10} 2 = \frac{2.303}{k} \times 0.3010 \end{aligned}$$

or

$$T_{1/2} = \frac{0.6932}{k}$$

Hence, half life period depends only upon disintegration constant of the radioactive element and does not depend upon initial concentration of radioactive substance.

If  $N_0$  is the initial concentration of radioactive substance and  $T_{1/2}$  is the half life period, then after time  $T_{1/2}$ , radioactive substance left behind will be  $N_0 \cdot (1/2)$ . After two half life periods ( $2T_{1/2}$ ), the amount of radioactive substance left behind will be  $N_0 \cdot (1/4)$  or  $N_0 (1/2)^2$ . Similarly, after  $n$  half life periods ( $nT_{1/2}$ ), the amount of radioactive substance left behind will be  $N_0 \cdot (1/2)^n$ .

Thus, after time  $t$ , i.e., after  $n$  half life periods ( $nT_{1/2}$ ), the amount of radioactive substance left behind is given by the relation:

$$N = N_0 \left( \frac{1}{2} \right)^n$$

i.e.,

$$t = n \times T_{1/2}$$

### • 5.4. AVERAGE LIFE PERIOD

Average life period or mean life period ( $\lambda$ ) is defined as the ratio of total life of all the radioactive atoms to the total number of such atoms present, i.e.,

$$\text{Average life period} = \frac{\text{Total life of all the radioactive atoms}}{\text{Total number of atoms}}$$

In other words, it is the time when a radioactive substance is completely disintegrated. If  $N_0$  is the initial amount of radioactive substance and  $N$  is the amount of radioactive substance left after time  $t$ , then we know that —

$$N = N_0 e^{-kt}$$

where  $k$  is the disintegration constant of radioactive substance.

$$\frac{N}{N_0} = e^{-kt}$$

Taking log —

$$\log_e \frac{N}{N_0} = -kt$$

or

$$\log_e \left( 1 - \frac{N_0 - N}{N_0} \right) = -kt$$

Expanding the above log series and neglecting higher powers of  $\frac{N_0 - N}{N_0}$

$$-\frac{N_0 - N}{N_0} = -kt$$

or

$$\frac{N_0 - N}{N_0} = kt$$

When radioactive substance is completely disintegrated, i.e.,  $N = 0$ , then  $t = \lambda$  (Average life period)

$$\frac{N_0 - 0}{N_0} = k\lambda$$

$$1 = k\lambda$$

$$\lambda = \frac{1}{k}$$

i.e., the reciprocal of disintegration constant is called as average life period.

We know that,  $T_{1/2} = \frac{0.6932}{k} = 0.6932 \times \lambda$

or

$$\lambda = \frac{1}{0.6932} \times T_{1/2} = 1.44 \times T_{1/2}$$

Average life period =  $1.44 \times$  Half life period.

**Ex. 1 :** The half life period of a radioactive element is 1600 years. Calculate its decay constant.

**Solution.**  $T_{1/2} = \frac{0.6932}{k}$

$$T_{1/2} = 1600 \text{ years}$$

$$1600 = \frac{0.6932}{k}$$

$$k = \frac{0.6932}{1600}$$

$$= 4.33 \times 10^{-4} \text{ years}^{-1}$$

**Ex. 2 :** The half life period of thorium is 20 days. In how many will days it be reduced to  $1/16$  of initial amount ?

**Solution.**  $N = N_0 \left(\frac{1}{2}\right)^n$

$$\frac{N_0}{16} = N_0 \left(\frac{1}{2}\right)^n$$

$$\frac{1}{16} = \left(\frac{1}{2}\right)^n \text{ or } \left(\frac{1}{2}\right)^4 = \left(\frac{1}{2}\right)^n$$

or

$$n = 4$$

$\therefore t = n \times T_{1/2} = 4 \times 20 = 80 \text{ days}$

**Ex. 3.** Half-life period of  $^{125}_{53}\text{I}$  is 60 days. What percentage of the original radioactivity would be present after 180 days ?

**Solution.**  $t = n \times T_{1/2}$

$$180 = n \times 60$$

$$n = \frac{180}{60} = 3$$

$$N = N_0 \times \left(\frac{1}{2}\right)^n$$

$$N = 100 \times \left(\frac{1}{2}\right)^3$$

$$= 100 \times \frac{1}{8}$$

$$= 12.5\%$$

**Ex. 4 :** Calculate the percentage mass left after 40 years of a radioactive substance if its half life period is 10 years.

**Solution.**

$$\begin{aligned}
 t &= n \times T_{1/2} \\
 40 &= n \times 10 \\
 n &= \frac{40}{10} = 4 \\
 N &= N_0 \times \left(\frac{1}{2}\right)^n \\
 N &= 100 \times \left(\frac{1}{2}\right)^4 \\
 &= 100 \times \frac{1}{16} = 6.25\%.
 \end{aligned}$$

**Ex. 5.** A radioactive nuclide decays to form a stable nuclide. Its half life period is 3 minutes. What fraction of 1 gm sample of the nuclide will remain radioactive after 9 minutes ?

**Solution.**

$$\begin{aligned}
 t &= n \times T_{1/2} \\
 9 &= n \times 3 \\
 n &= \frac{9}{3} = 3 \\
 N &= N_0 \times \left(\frac{1}{2}\right)^n \\
 &= 1 \times \left(\frac{1}{2}\right)^3 \\
 &= \frac{1}{8} \text{ gm.}
 \end{aligned}$$

Hence, fraction of 1 gm sample of the nuclide remaining radioactive =  $\frac{1}{8}$ .

**Ex. 6:** The radioactivity of a radioactive isotope is reduced to 12.5% in 90 days. Calculate its half life period and decay constant.

**Solution.**

$$\begin{aligned}
 N &= N_0 \times \left(\frac{1}{2}\right)^n \\
 \frac{12.5}{100} N_0 &= N_0 \times \left(\frac{1}{2}\right)^n \\
 \frac{1}{8} &= \left(\frac{1}{2}\right)^n \\
 \left(\frac{1}{2}\right)^3 &= \left(\frac{1}{2}\right)^n
 \end{aligned}$$

 $\therefore$ 

$$n = 3$$

But

$$t = n \times T_{1/2}$$

$$90 = 3 \times T_{1/2}$$

$$T_{1/2} = 30 \text{ days}$$

$$T_{1/2} = \frac{0.6932}{k}$$

$$30 = \frac{0.6932}{k}$$

or

$$k = \frac{0.6932}{30}$$

$$= 2.310 \times 10^{-2} \text{ days}^{-1}$$

**Ex. 7:** The rate of decay of radioactive element changes from 48 dps to 28 dps in 60 days. Calculate the half life period of the radioactive element.

**Solution.** We have  $t = 60$  days

$$N = N_0 \times \left(\frac{1}{2}\right)^n$$

$$28 = 48 \times \left(\frac{1}{2}\right)^n$$

or

$$\left(\frac{1}{2}\right)^n = \frac{28}{48}$$

or

$$\left(\frac{1}{2}\right)^n = \frac{7}{12}$$

or

$$2^n = \frac{12}{7}$$

$$n \log 2 = \log 12 - \log 7$$

$$n \times 0.3010 = 1.0792 - 0.8451$$

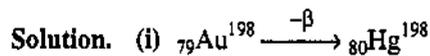
$$n = \frac{0.2341}{0.3010}$$

$$t = n \times T_{1/2}$$

$$60 = \frac{0.2341}{0.3010} \times T_{1/2}$$

$$T_{1/2} = \frac{60 \times 0.3010}{0.2341} = 77.14 \text{ days}$$

**Ex. 8 :** 1 gm of  ${}_{79}\text{Au}^{198}$  ( $T_{1/2} = 65$  hours) emits a  $\beta$ -particle and gives stable isotope of Hg. Calculate the amount of Hg after 260 hours.



(ii)  $T_{1/2} = 65$  hours,

$\therefore t = 260$  hours

But  $t = n \times T_{1/2}$

or  $260 = n \times 65$  or  $n = 4$

$N_0 = 1$  gram

$$N = N_0 \times \left(\frac{1}{2}\right)^n$$

$$= 1 \times \left(\frac{1}{2}\right)^4 = \frac{1}{16}$$

Amount of gold left =  $\frac{1}{16}$

Amount of mercury present =  $1 - \frac{1}{16} = \frac{15}{16} = 0.9375$  gram.

**Ex. 9 :** The disintegration rate of some radioactive substance at any instant was 4750 dpm. Five minutes later the rate becomes 2700 dpm. Calculate half life period of radioactive substance.

**Solution.** We know that  $N = N_0 \times \left(\frac{1}{2}\right)^n$

$$2700 = 4750 \times \left(\frac{1}{2}\right)^n$$

$$\left(\frac{1}{2}\right)^n = \frac{2700}{4750}$$

$$2^n = \frac{4750}{2700} = \frac{475}{270}$$

$$n \log 2 = \log 475 - \log 270$$

$$= 2.6767 - 2.4314$$

$$n \times 0.3010 = 0.2453$$

$$n = \frac{0.2453}{0.3010}$$

$$t = n \times T_{1/2}$$

$$5 = \frac{0.2453}{0.3010} \times T_{1/2}$$

$$T_{1/2} = \frac{5 \times 0.3010}{0.2453}$$

$$= 6.135 \text{ minutes.}$$

**Ex. 10 :** Half life period of Kr-85 is 10.6 years. How long will it take for 99% of this element to disintegrate?

**Solution.** We know that,

$$k = \frac{0.6932}{T_{1/2}} = \frac{0.6932}{10.6} = 0.065$$

$$t = \frac{2.303}{k} \log_{10} \frac{a}{a-x}$$

For 99% of the element to disintegrate,  $x = 0.99a$

$$t = \frac{2.303}{0.065} \log_{10} \frac{a}{a - 0.99a}$$

$$t = \frac{2.303}{0.065} \log_{10} \frac{1}{0.01} = \frac{2.303}{0.065} \log_{10} 100$$

$$= \frac{2.303}{0.065} \times 2 = 70.8 \text{ years.}$$

Ex. 11 : One gram of a radioactive isotope of sodium decays to 0.25 gram in 20 hours. How much time will it take for 90% disintegration?

Solution. We know that,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a - x}$$

$t = 20$  hours,  $a = 1$  gram,  $a - x = 0.25$  gram

$$k = \frac{2.303}{20} \log_{10} \frac{1}{0.25}$$

$$= \frac{2.303}{20} \log_{10} 4 = \frac{2.303 \times 0.6021}{20}$$

$$t = \frac{2.303}{k} \log_{10} \frac{a}{a - x}$$

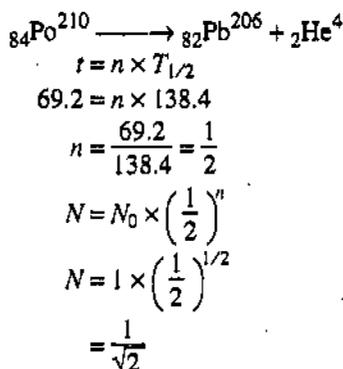
$$k = \frac{2.303 \times 0.6021}{20}, x = \frac{90}{100} a$$

$$t = \frac{2.303 \times 20}{2.303 \times 0.6021} \log_{10} \frac{a}{a - \frac{90}{100} a}$$

$$= \frac{20}{0.6021} \log_{10} 10 = \frac{20}{0.6021} = 33.21 \text{ hours.}$$

Ex. 12 :  ${}_{84}\text{Po}^{210}$  decays with  $\alpha$ -particle to  ${}_{82}\text{Pb}^{206}$  with a half life period of 138.4 days. If 1 gm of polonium is placed in a sealed tube, how much helium would accumulate in 69.2 days at S.T.P. ?

Solution.



Amount of polonium left after

$$69.2 \text{ days} = \frac{1}{\sqrt{2}} \text{ gm.}$$

Amount of polonium decomposed to give helium

$$= 1 - \frac{1}{\sqrt{2}} = \frac{\sqrt{2} - 1}{\sqrt{2}} \text{ gm.}$$

$$= \frac{1.414 - 1}{1.414} = \frac{0.414}{1.414}$$

$$= 0.2928 \text{ gm.}$$

$\therefore$  210 gm of polonium gives helium = 4 gm = 22400 cc at S.T.P.

$$\therefore 0.2928 \text{ gm of polonium gives helium} = \frac{22400 \times 0.2928}{210}$$

$$= 31.23 \text{ c.c.}$$

Ex. 13 : A carbon radioactive isotope  ${}_Z\text{X}^A$  ( $T_{1/2} = 10$  days) decays to give  ${}_{Z-2}\text{Y}^{A-4}$ . If one gram atom of  ${}_Z\text{X}^A$  is kept in a sealed tube, how much helium will be produced in 20 days at S.T.P.?







$$\frac{0.6932}{T_a} \times n_a = \frac{0.6932}{T_b} \times n_b = \frac{0.6932}{T_c} \times n_c$$

or 
$$\frac{n_a}{T_a} = \frac{n_b}{T_b}$$

or 
$$\frac{n_a}{n_b} = \frac{T_a}{T_b} = \frac{\lambda_b/1.44}{\lambda_a/1.44}$$

or 
$$\frac{n_a}{n_b} = \frac{T_a}{T_b} = \frac{\lambda_b}{\lambda_a}$$

Thus, in radioactive equilibrium the ratio of the number of atoms is the same as the ratio of their half life periods or average life periods.

Radioactive equilibrium differs from chemical equilibrium in the following respects :

(i) Radioactive equilibrium is an irreversible reaction whereas chemical equilibrium is a reversible reaction.

(ii) Radioactive equilibrium is not affected by physical factors such as pressure, temperature whereas chemical equilibrium is affected by physical factors.

**Ex. 1 :** *At radioactive equilibrium the ratio between atoms of two radioactive elements A and B was found to be  $3.1 \times 10^9 : 1$ . If the half life period of A is  $2 \times 10^{10}$  years, what is the half life period of element B?*

**Solution.** For radioactive equilibrium,

$$\frac{n_a}{n_b} = \frac{T_a}{T_b}$$

$$\frac{3.1 \times 10^9}{1} = \frac{2 \times 10^{10}}{T_b}$$

or 
$$T_b = \frac{2 \times 10^{10}}{3.1 \times 10^9} = \frac{20}{3.1} = 6.451 \text{ years.}$$

## • 5.7. ARTIFICIAL DISINTEGRATION OR TRANSMUTATION OF ATOMS

In the natural radioactive changes there occurs a spontaneous disintegration of unstable nucleus with the emission of radioactive radiations. This process continues until a stable atom is produced. In these changes, neither the rate of disintegration nor the nature of radioactive radiations can be controlled.

After this, attempts were made in the laboratory to disintegrate stable atoms by bombarding the nuclei with fast moving small high energy particles so as to obtain the new atoms. *This phenomenon, in which the stable atoms are disintegrated by artificial means, is known as artificial disintegration of atoms.*

Rutherford, in 1919, first of all bombarded stable nitrogen atoms with high speed  $\alpha$ -particles and obtained traces of oxygen.

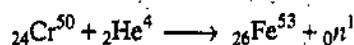


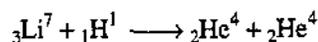
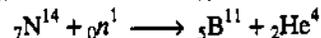
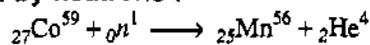
In addition to the  $\alpha$ -particles, some other atomic particles such as protons, deuterons and neutrons are also used as bombarding particles for the purpose of artificial disintegration. Since  $\alpha$ -particles carry double positive charge, they are not good bombarding particles for the said purpose, because they are repelled by the positively charged nucleus. Protons and deuterons, which carry single positive charge, are much better bombarding particles as compared to  $\alpha$ -particles. Neutrons, being neutral, are very useful because they are not repelled or attracted by the nuclei of atoms.

The positively charged  $\alpha$ -particles, deuterons and protons can be made much more effective by increasing their velocity. The apparatus used for the purpose is known as **cyclotron**. This increase in velocity results in the high kinetic energy which overcomes the forces of repulsion between the positively charged nucleus and the bombarding particles. However, in such bombardments the total positive charge and total mass before and after the bombardment should be balanced.

A few examples of artificial disintegration of atoms are as follows :

(i) **Disintegration by  $\alpha$ -particles :**



**(ii) Disintegration by protons :****(iii) Disintegration by deuterons :****(iv) Disintegration by neutrons :**

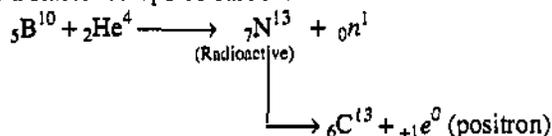
The energy liberated during the process of artificial disintegration can be utilized for different purposes. The atom bomb is an application of artificial disintegration of atoms.

## • 5.8. ARTIFICIAL RADIOACTIVITY

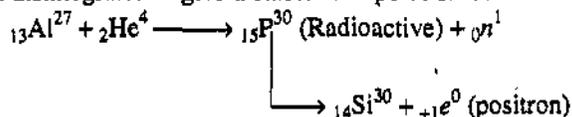
In the artificial disintegration of atoms, as soon as the bombarding particles are removed, the process of disintegration also stops. In 1939, Joliot and his wife Irene Curie observed that bombardment of  $\alpha$ -particles on certain light elements such as boron, magnesium and aluminium gives rise to radioactive isotopes of other elements. These isotopes disintegrate just as the naturally occurring radioactive substances like radium, thorium etc. do.

Thus, the phenomenon by which a stable element is changed into radioactive element by the process of artificial disintegration is known as artificial radioactivity.

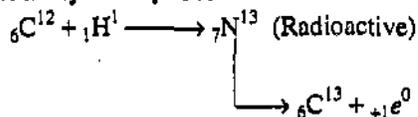
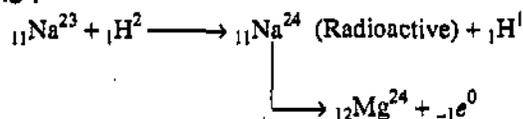
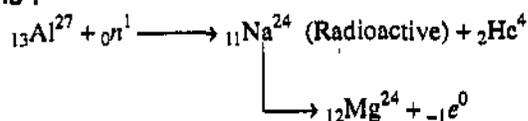
Thus, boron on bombardment with  $\alpha$ -particles, gives a radioactive isotope of nitrogen which then disintegrates to give a stable isotope of carbon.



Similarly, aluminium on bombardment with  $\alpha$ -particles gives a radioactive isotope of phosphorus which then disintegrates to give a stable isotope of silicon.



The protons, deuterons accelerated by cyclotron and neutrons also give rise to radioactive isotopes.

**Artificial radioactivity with protons :****With deuterons :****With neutrons :****Applications of artificial radioactivity :**

(i) In the preparation of transuranic elements, i.e., the elements after uranium.

(ii) In the preparation of elements with atomic numbers 43, 61, 85 and 87. These elements

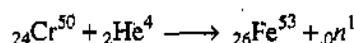
were unknown at the time of Mendeleef.

(iii) The artificially prepared radioactive isotopes are very much used in medicines, agriculture and in biological fields.

## • 5.9. NUCLEAR REACTIONS

The reactions, in which the nuclei of the atoms are disintegrated into new nuclei either by themselves or by bombarding with fast moving small high energy particles, are called **nuclear reactions**. These reactions are represented just like ordinary chemical reactions, *i.e.*, the reactants are written on the left side and products on the right side. In addition, in these reactions, the atomic numbers of reactants and products are written as the subscript and atomic mass as the superscript. The important point is that the total positive charge and total atomic mass before and after the bombardment should be balanced. Like symbols for the atoms of the elements, the bombarding particles are also represented by the following symbols :  ${}_2\text{He}^4$  for  $\alpha$ -particle,  ${}_0n^1$  for neutron,  ${}_1\text{H}^1$  or  $p$  for proton,  ${}_{-1}e^0$  for electron,  ${}_{+1}e^0$  for positron,  ${}_1\text{H}^2$  or  $d$  for deuteron etc.

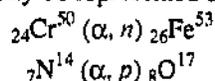
The various types of nuclear reactions may be represented as  $(\alpha, n)$ ,  $(p, \alpha)$ ,  $(d, p)$ ,  $(d, n)$ ,  $(n, \alpha)$  etc. In these, the first letter stands for bombarding particle and second letter indicates the ejected particle. For example, the following nuclear reaction is  $(\alpha, n)$  type



Similarly, the following reaction is  $(\alpha, p)$  type :

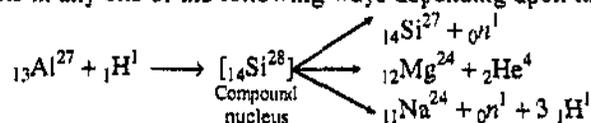


Sometimes, the nuclear reactions are also represented by short hand method. For example, the above nuclear reactions may be represented as—



### [I] Bohr's Theory of Nuclear Reactions

According to this theory, the bombarding particle combines with the nucleus to be bombarded to form a compound nucleus which is now in the excited state. This excited nucleus has small life period ( $10^{-12}$  to  $10^{-14}$  sec) and, therefore, breaks up to give the final product with the release of energy. The nature of the final product depends upon the energy of the compound nucleus. For example, when  ${}_{13}\text{Al}^{27}$  is bombarded with protons, a compound nucleus  ${}_{14}\text{Si}^{28}$  is formed which may disintegrate in any one of the following ways depending upon its energy.

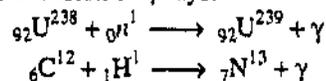


### [II] Classification of Nuclear Reactions

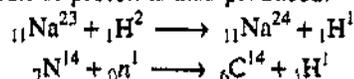
#### (1) Based on energy

This type of nuclear reactions are based upon overall energy transformation. These are :

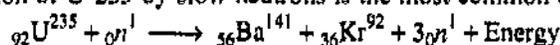
(a) **Capture reactions** : These are the reactions, in which the bombarding particle is absorbed with or without the emission of  $\gamma$ -rays.



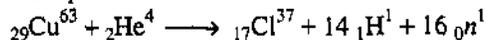
(b) **Particle-particle reactions** : These are the reactions, in which the bombarding particle is absorbed to form the compound nucleus which then breaks into the product nucleus and a massive nucleus like neutron or proton is also produced.



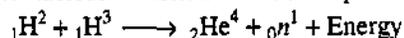
(c) **Fission reactions** : These are the reactions, in which the bombarding particle is absorbed to form the compound nucleus which then breaks up into two massive nuclei of somewhat the same size with or without the emission of light particles. In such reactions, a large amount of energy is liberated. The fission of U-235 by slow neutrons is the most common example.



(d) **Spallation reactions** : These are the reactions, in which the bombarding particle is absorbed to form the compound nucleus which then breaks up to form a normal nucleus and a large number of light particles. This type of reactions were discovered by G.T. Seaborg and J. Periman in 1947. The bombardment of high speed  $\alpha$ -particles on Cu-63 to form Cl-37 along with 14 protons and 16 neutrons is an example.

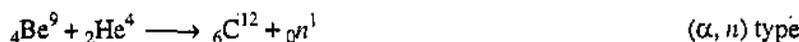


(e) **Fusion reactions** : These are the reactions, in which two light nuclei fuse together to form a heavy nucleus with the liberation of tremendous amount of energy. The fusion of deuterium and tritium to form a stable nucleus of helium is an example.



## (2) Based on nature of bombarding particle

### (a) Alpha Induced reactions :



### (b) Proton induced reactions :



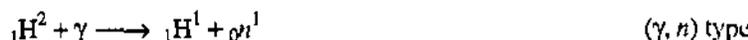
### (c) Deuteron induced reactions :



### (d) Neutron induced reactions :

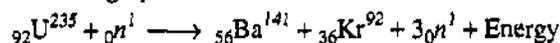


### (e) Gamma induced reactions :



## • 5.10. NUCLEAR FISSION (ATOMIC FISSION)

Hahn and Strassmann in 1939, observed that when uranium-235 is bombarded with slow neutrons, a neutron is first of all captured by the uranium nucleus and then it breaks up into two nuclei— ${}_{56}\text{Ba}^{141}$  and  ${}_{36}\text{Kr}^{92}$ —of somewhat the same size. Out of three isotopes of uranium,  $\text{U}^{235}$  is present to the extent of 0.7% only. The speed of the neutrons is reduced by passing them through a moderator, e.g., heavy water or graphite.



The phenomenon of splitting up of nucleus of heavy atom into two nuclei of somewhat the same size with the liberation of huge amount of energy is known as nuclear fission.

The secondary neutrons, which are produced, strike against other uranium atoms thus, causing more fission along with release of more neutrons and more energy. Thus, this process continues in the form of a chain reaction and ultimately an explosion results on account of tremendous amount of energy. This is the principle of an atom bomb.

Recent researches have shown that uranium is not the only element which undergoes fission. It has been found that elements having atomic number  $\geq 85$  undergo fission with suitable energy neutrons. Moreover, fission is also possible with other bombarding particles such as protons, deuterons,  $\alpha$ -particles and  $\gamma$ -rays.

During nuclear fission, there occurs some loss of mass which is responsible for the liberation of tremendous amount of energy given by Einstein's relation,  $E = mc^2$ . In the fission of U-235, there occurs a loss of 0.2 units of mass per gram atom of uranium and this loss amounts to  $0.2 \times (3 \times 10^{10})^2$  ergs of energy.

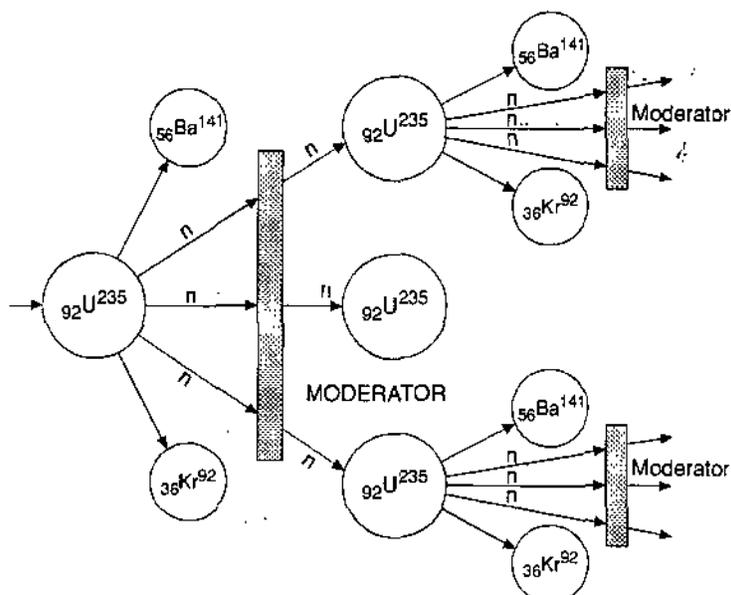
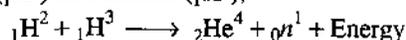


Fig. 3. Chain reaction in nuclear fission.

Now-a-days, this chain reaction is controlled by nuclear reactor and the liberated energy is utilized for power production.

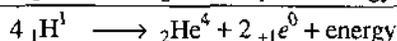
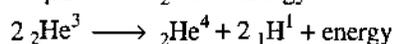
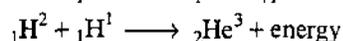
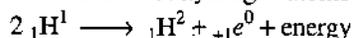
### • 5.11. NUCLEAR FUSION (ATOMIC FUSION)

The process which involves the fusion or combination of two lighter nuclei to give a somewhat heavier and more stable nucleus with the liberation of tremendous amount of energy is known as nuclear fusion. This is the principle of hydrogen bomb. The two light nuclei employed for the purpose are isotopes of hydrogen, i.e., deuterium ( ${}_1\text{H}^2$ ) and tritium ( ${}_1\text{H}^3$ ).



The positively charged atomic nuclei on account of forces of repulsion do not fuse at ordinary temperature. At very high temperatures, the nuclei may have sufficient energy to overcome the forces of repulsion and thus, they fuse. These reactions, are, therefore, also called *thermo-nuclear reactions*. The high temperature needed is brought about by a bomb of fission type.

The energy of the sun is also due to fusion of hydrogen atoms to form a stable helium nucleus.



In these reactions, there also occurs a loss of 0.4 unit mass which is responsible for the liberation of tremendous amount of energy given by Einstein's relation,  $E = mc^2$ . However, the loss of mass in this case is greater than in the fission reactions.

Hydrogen bomb is thousand times more destructive than fission type of atomic bombs, because in these reactions the energy liberated is much more than in the fission reactions.

#### [1] Difference between Nuclear Fission and Nuclear Fusion

	Nuclear fission	Nuclear fusion
1.	It involves the splitting up of nucleus of heavy atom into two or more lighter nuclei $92\text{U}^{235} + {}_0n^1 \rightarrow 56\text{Ba}^{141} + 36\text{Kr}^{92} + 3 {}_0n^1 + \text{energy}$	It involves the fusion or combination of two or more lighter nuclei to give a heavier and more stable nucleus, ${}_1\text{H}^2 + {}_1\text{H}^3 \rightarrow {}_2\text{He}^4 + {}_0n^1 + \text{Energy}$
2.	It does not require high temperature.	It requires very high temperature.
3.	It is a chain reaction.	It is not a chain reaction.
4.	It can be controlled and liberated energy can be used for power production.	It can not be controlled and liberated energy can not be properly used.
5.	The products formed are radioactive.	The products formed are non radioactive.
6.	The energy released is less as compared to nuclear fusion.	The energy released is much higher than nuclear fission.

## • 5.12. APPLICATIONS OF RADIOACTIVE ISOTOPES

(i) **As tracers** : The radioactive isotopes are very much used as tracers, *i.e.*, for studying the mechanism of various reactions. For example, radioactive carbon, *i.e.*,  $C^{14}$  is used for studying the mechanism of photosynthesis in plants. It is also used in studying the mechanisms involved in alkylation, catalytic cracking, polymerization.

(ii) **In medicines** :

(a) Radioactive cobalt ( $Co^{60}$ ) and radium are used for the treatment of cancer.

(b) Radioactive iodine ( $I^{131}$ ) is used for locating brain tumour and also to determine the extent of its growth.

(c) Radioactive sodium, *i.e.*,  $Na^{24}$  is used to study blood circulation.

(d) Radioactive phosphorus ( $P^{32}$ ) in the form of phosphates is used for the treatment of blood disorders.

(iii) **In the determination of solubility of sparingly soluble salts** : The solubility of sparingly soluble salts such as  $PbSO_4$  or  $PbCrO_4$  in water can be determined by mixing a known quantity of radioactive isotope of lead to known quantity of ordinary lead. The activity of the mixed solid is determined. The mixture is now dissolved in nitric acid and solution of lead nitrate so obtained is treated with  $K_2CrO_4$  or  $H_2SO_4$  to obtain the precipitate of  $PbCrO_4$  or  $PbSO_4$ . This precipitate is now filtered off. The quantity of  $PbCrO_4$  or  $PbSO_4$  still in solution can be determined by measuring the radioactivity per ml of the solution.

(iv) **In agriculture** : Radioactive isotopes are used to find ways to increase the crop yield. The  $\gamma$ -rays obtained by the decay of  $Co^{60}$  increase the yield and quality of crops. Radioactive phosphorus is used to trace the uptake of phosphorus by plants.

(v) **In industry** : Radioactive isotopes are used to measure the thickness of sheet of paper, steel, rubber etc. They are also used to determine the surface area of solids and age of rocks and minerals.  $C^{14}$  is used to determine the life period of vegetable ghee.

(vi) **In biological fields** : Radioactive isotopes are used to study metabolic interconversions in the body. They are also used to study the mechanism of various biological processes, *i.e.*, the movement of ions across the cell membrane.

(vii) **In dating** : Radioactive isotopes are used to estimate the age of earth, geological, archeological and biological specimens. For example, age of earth is determined by uranium dating technique, whereas age of archeological and biological specimens is determined by carbon dating technique.

(a) **Determination of age of rocks and minerals (uranium dating)** : The rocks and minerals generally contain radioactive elements. These radioactive elements disintegrate and finally give a stable end product. Each disintegration step has a definite half life period and decay constant. Thus, a rock or mineral may contain the remaining parent radioactive element and the end product formed. If the ratio of the amounts of end product and that of parent radioactive element in the given sample is known, the age of rocks and minerals can be calculated.

Suppose we have to determine the age of rock containing  ${}_{92}U^{238}$  ( $T_{1/2} = 4.5 \times 10^9$  years).  ${}_{92}U^{238}$  is a member of  $(4n + 2)$  series and disintegrates to give the end product  ${}_{82}Pb^{206}$ . Since half life period of  ${}_{92}U^{238}$  is much higher than that of any other member of the series, it is assumed that all  ${}_{82}Pb^{206}$  has been obtained by the disintegration of  ${}_{92}U^{238}$  and the rock initially did not contain any lead. If  $N_0$  is the initial amount of  ${}_{92}U^{238}$  and  $N$  is the amount of  ${}_{92}U^{238}$  left at the time of analysis, the age of rock  $t$  can be calculated by the relation –

$$t = \frac{2.303}{k} \log_{10} \frac{N_0}{N}$$

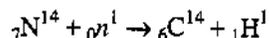
where  $k$  is disintegration constant of  ${}_{92}U^{238}$  and can be calculated by –

$$k = \frac{0.6932}{T_{1/2}}$$

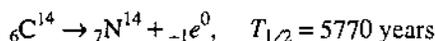
where  $T_{1/2}$  is the half life period of  ${}_{92}U^{238}$ .

(b) **Determination of age of archeological and biological specimens (carbon dating)** : The age of a piece of wood and an animal fossil can be determined by radio carbon dating technique. The technique was developed by W.F. Libby. The technique is based on the fact that all

living matters (plants and animals) contain a definite amount of radioactive isotope,  ${}_6\text{C}^{14}$ . It is formed in the upper atmosphere by the bombardment of neutrons (produced by cosmic rays) on  ${}_{7}\text{N}^{14}$ .



The amount of  ${}_6\text{C}^{14}$  in the atmosphere is very small but it can be easily detected and estimated because of its radioactive nature. It is oxidized in the air to give radioactive  $\text{CO}_2$ . Thus, atmospheric  $\text{CO}_2$  also contains very small amount of radioactive  $\text{CO}_2$  ( $\text{C}^{14}\text{O}_2$ ). It is absorbed by living plants and through them by animals also. When plant or animal dies, fresh  ${}_6\text{C}^{14}$  as  $\text{C}^{14}\text{O}_2$  is not received by the plant or animal. The  $\text{C}^{14}$  present in them continuously decays as follows —



The amount of  $\text{C}^{14}$  in a sample can be determined by counting the number of  $\beta$ -particles emitted per minute by one gram of the sample. Thus, by knowing the amount of  $\text{C}^{14}$  in a living matter and in a dead piece of matter, the age of the sample can be determined. If  $N_0$  is the initial  $\text{C}^{14}$  content in a living plant or animal and  $N$  is  $\text{C}^{14}$  content left at the time of analysis, the age  $t$  of plant or animal can be calculated by the relation —

$$t = \frac{2.303}{k} \log_{10} \frac{N_0}{N}$$

where  $k$  is disintegration constant of  ${}_6\text{C}^{14}$  and can be calculated by

$$k = \frac{0.6932}{T_{1/2}}$$

where  $T_{1/2}$  is half life period of  ${}_6\text{C}^{14}$ .

**Ex. 1 :** The amount of  $\text{C}^{14}$  in a sample of wood is found to be one fourth of the amount present in a fresh piece of wood. Calculate the age of the wood. ( $t_{0.5} = 5770$  years).

**Solution.**  $T_{1/2} = 5770$  years

$$N = N_0 \times \left(\frac{1}{2}\right)^n$$

$$\frac{N_0}{4} = N_0 \times \left(\frac{1}{2}\right)^n$$

or 
$$\frac{1}{4} = \left(\frac{1}{2}\right)^n \quad \therefore n = 2$$

$$t = n \times T_{1/2} = 2 \times 5770 = 11540 \text{ years}$$

**Problem 2 :**  ${}_{92}\text{U}^{238}$  by successive radioactive decays changes to  ${}_{82}\text{Pb}^{206}$ . A sample of uranium ore was analysed and found to contain 1 gm of  ${}_{92}\text{U}^{238}$  and 0.1 gm of  ${}_{82}\text{Pb}^{206}$ . Assuming that all the  ${}_{82}\text{Pb}^{206}$  has been obtained due to decay of uranium, find out the age of uranium mineral. ( $T_{1/2}$  of  $\text{U}^{238} = 4.5 \times 10^9$  years).

**Solution.** Assuming that all the  ${}_{82}\text{Pb}^{206}$  has been obtained due to decay of  ${}_{92}\text{U}^{238}$ .

$\therefore$  206 gm Pb is obtained from 238 gm of uranium

$\therefore$  0.1 gm Pb is obtained from

$$= \frac{238}{206} \times 0.1 = 0.1155 \text{ gm.}$$

Hence initial amount of  ${}_{92}\text{U}^{238} = 1 + 0.1155$

$$= 1.1155 \text{ gm}$$

Amount of  ${}_{92}\text{U}^{238}$  present at the time of analysis = 1.0 gm.

$$t = \frac{2.303}{k} \log_{10} \frac{N_0}{N}$$



2. Define half life period and average life period.

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3. Write a note on nuclear fission.

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4. Describe two applications of radioactive isotopes.

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### • TEST YOURSELF

Answer the following questions :

1. Define natural radioactivity. Describe the properties of radioactive rays.
2. Write the unit of radioactivity.
3. In what respects are radioactive changes different from ordinary chemical changes.
4. Explain the theory of radioactive disintegration.
5. State and explain group displacement law.
6. Show that the rate of radioactive decay is a first order reaction.
7. Define half life period and average life period of a radioactive element. Deduce the formula for their determination. How are they related to each other ?
8. Write short notes on the following :
  - (a) Radioactive disintegration series
  - (b) Radioactive equilibrium
  - (c) Artificial disintegration of atoms
  - (d) Artificial radioactivity
9. What are nuclear reactions ? Give their classification.
10. Discuss the following with suitable examples :
  - (a) Nuclear fission
  - (b) Nuclear fusion
11. What are the differences between nuclear fission and nuclear fusion ?
12. Describe the applications of radioactive isotopes.
13. The radioactivity changes with :
  - (a) Temperature
  - (b) Pressure

- (c) Chemical environment (d) None of these
14.  ${}_{92}\text{U}^{235}$  belongs to group III B of periodic table. If it loses one  $\alpha$ -particle, the new element belongs to the group :  
 (a) IB (b) IA (c) IIIB (d) VB
15.  ${}_{92}\text{U}^{235}$  is parent of a radioactive decay series which terminates at  ${}_{82}\text{Pb}^{207}$ . The total number of  $\alpha$  and  $\beta$ -particles emitted are :  
 (a)  $8\alpha + 6\beta$  (b)  $7\alpha + 2\beta$   
 (c)  $7\alpha + 4\beta$  (d)  $6\alpha + 4\beta$
- Radioactive disintegration of tritium gives :  
 (a)  $\alpha$ -particles (b)  $\beta$ -particles  
 (c) Neutrons (d) None
17. After two hours, one-sixteenth of original quantity of radioactive substance remains undecayed. The half life period of the substance is:  
 (a) 15 minutes (b) 30 minutes  
 (c) 45 minutes (d) 60 minutes
18. Atom bomb is based on the principle of :  
 (a) Nuclear fission (b) Radioactivity  
 (c) Nuclear fusion (d) None of these.
19. The appreciable radioactivity of uranium mineral pitch blende ( $\text{U}_3\text{O}_8$ ) is due to :  
 (a) Uranium (b) Thorium  
 (c) Radium (d) Plutonium
20. In  $\beta$ -decay :  
 (a)  $n/p$  increases (b)  $n/p$  decreases  
 (c)  $n/p$  remains constant  
 (d)  $n/p$  may increase or decrease as the case may be.
21. Which of the following particles is used to bombard  ${}_{13}\text{Al}^{27}$  to give  ${}_{15}\text{P}^{30}$  and a neutron ?  
 (a)  $\alpha$ -particle (b) proton  
 (c) deuteron (d) neutron
22. If 8 gm of a radioactive isotope has a half life of 10 hours, the half life of 2 gm of the same substance is :  
 (a) 2.5 hrs. (b) 5 hrs.  
 (c) 10 hrs. (d) 40 hrs.
- The number of  $\alpha$ - and  $\beta$ -particles emitted in the nuclear reaction  ${}_{90}\text{Th}^{228} \longrightarrow {}_{83}\text{Bi}^{212}$  are :  
 (a)  $4\alpha + 1\beta$  (b)  $3\alpha + 7\beta$   
 (c)  $8\alpha + 1\beta$  (d)  $4\alpha + 7\beta$
24. The half life period of a radioactive element is 140 days. After 560 days, one gram of the element will reduce to :  
 (a)  $\frac{1}{2}$  gm (b)  $\frac{1}{4}$  gm  
 (c)  $\frac{1}{8}$  gm (d)  $\frac{1}{16}$  gm
25.  ${}_{7}\text{N}^{13}$  changes to  ${}_{6}\text{C}^{13}$  by emission of :  
 (a) electron (b) proton  
 (c) neutron (d) positron
26. In  $\alpha$ -decay :  
 (a)  $\frac{n}{p}$  increases (b)  $\frac{n}{p}$  decreases  
 (c)  $\frac{n}{p}$  remains constant  
 (d)  $\frac{n}{p}$  may increase or decrease as the case may be.
37. Fill in the Blanks :  
 (i) The last element obtained in thorium series is .....  
 (ii) The isotope used to find out the age of rocks is .....  
 (iii) The parent nucleus which gives nitrogen on  $\beta$ -emission is .....  
 (iv) The last element obtained in actinium series is .....  
 (v) A radioactive element has decay constant  $6.93 \times 10^{-3} \text{ sec}^{-1}$ . Its half life is ..... sec.

- (vi) The instrument for measuring and detecting radioactivity is .....
- (vii) The element obtained by the radioactive disintegration of tritium is .....
- (viii) The last element obtained in neptunium series is .....
- (ix) The emission of a  $\beta$ -particle results in the formation of an .....
- (x) The substance which can slow down the speed of neutrons without absorbing them, is known as .....
- (xi) A radioactive isotope emits one  $\alpha$ - and two  $\beta$ -particles, the resulting nucleus is ..... of the parent.
- (xii) A radioactive isotope  ${}_Z X^A$  emits one  $\alpha$ - and two  $\beta$ -particles, the resulting element formed is .....

28.

Match the following :

(a)	Group displacement law	(1)	Nuclear fusion
(b)	Thermonuclear reaction	(2)	Soddy
(c)	Artificial radioactivity	(3)	Marie Curie
(d)	Radium	(4)	Irene Curie
(e)	Theory of nuclear reaction	(5)	Rutherford
(f)	Artificial disintegration of atoms	(6)	Neil Bohr

### ANSWERS

13. (d); 14. (c); 15. (c); 16. (b); 17. (b); 18. (a); 19. (c); 20. (b); 21. (a), 22. (c); 23. (a); 24. (d); 25. (d); 26. (a).

27. Fill in the blanks :

(i)  ${}_{82}\text{Pb}^{208}$  (ii)  ${}_{92}\text{U}^{238}$  (iii)  ${}_6\text{C}^{14}$  (iv)  ${}_{82}\text{Pb}^{207}$  (v) 10 sec. (vi) G.M. Counter  
 (vii)  ${}_2\text{He}^3$  (viii)  ${}_{83}\text{Bi}^{209}$  (ix) isobar (x) moderator (xi) isotope (xii)  ${}_Z X^{A-4}$

IV. Match the following :

(a) Group displacement law	(2) Soddy
(b) Thermonuclear reaction	(1) Nuclear Fusion
(c) Artificial radioactivity	(4) Irene Curie
(d) Radium	(3) Marie Curie
(e) Theory of nuclear reaction	(6) Neil Bohr
(f) Artificial disintegration of atom	(5) Rutherford



## 6

CHEMISTRY OF ELEMENTS OF FIRST,  
SECOND AND THIRD TRANSITION

## STRUCTURE

- Transition Elements
- General Properties of Elements of First Transition Series
- Comparative Study of Elements of Second and Third Transition Series
- Explanation of facts with reason,
  - Summary
  - Student Activity
  - Test Yourself

## LEARNING OBJECTIVES

After going this unit you will learn :

- Different transition series and electronic configuration.
- Formation of coloured and complex salts.
- Spin magnetic moment of a single unpaired electron and an atom ion or molecule
- Formation of non-stoichiometric and interstitial compounds.
- Elements of 2nd and 3rd transition series.

## 6.1. TRANSITION ELEMENTS

These are the elements with atoms in which two outermost shells are incomplete, whereas all the rest shells are complete. The atoms of these elements have general electronic configuration of their two outermost shells as  $(n-1)s^2, (n-1)p^6, (n-1)d^{1-9}, ns^{1-2}$ . The elements of the groups I B, II B, ... VII B and VIII group belong to this class. These elements are characterised by the regular filling of  $d$ -sub-energy level of their electronic configuration, therefore, these are also called as  $d$ -block elements. Thus, transition elements may also be defined as the elements whose atoms or simple ions contain partially filled  $d$ -orbitals. This definition does not include Zn, Cd and Hg in the category of transition elements as these elements contain completely filled  $d$ -orbitals in their elementary and commonly occurring ions. However, these are  $d$ -block elements as there is a regular filling of  $d$ -subenergy level of their electronic configuration. Because of the regular filling of  $3d, 4d, 5d$  or  $6d$  subenergy levels, there are four series of transition elements :

**First Transition or  $3d$  Series :** In this series, there is a regular filling of  $3d$  subenergy level. This series contains ten elements  $_{21}\text{Sc}$  to  $_{30}\text{Zn}$ .

TRANSITION ELEMENTS d-BLOCK									
IIB	IVB	VB	VIB	VII B	VIII			IB	IIB
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
21	22	23	24	25	26	27	28	29	30
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
39	40	41	42	43	44	45	46	47	48
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
57	72	73	74	75	76	77	78	79	80
Ac	Ku	Ha	Sg	Bh	Hs	Mt			
89	104	105	106	107	108	109			

**Second Transition or  $4d$  Series :** In this series, there is a regular filling of  $4d$  subenergy level. This series contains ten elements  $_{39}\text{Y}$  to  $_{48}\text{Cd}$ .

**Third Transition or  $5d$  Series :** In this series, there is a regular filling of  $5d$  subenergy level. This series also contains ten elements from  $_{57}\text{La}$  to  $_{80}\text{Hg}$  except 14 elements of lanthanide series from  $_{58}\text{Ce}$  to  $_{71}\text{Lu}$  which have been placed below the main part of the periodic table.

**Fourth Transition or 6d Series :** In this series, there is a regular filling of 6d subenergy level. This series is incomplete and contains seven elements from  $_{89}\text{Ac}$  to  $_{109}\text{Mt}$  except 14 elements of actinide series from  $_{90}\text{Th}$  to  $_{103}\text{Lw}$  which have been placed below the main part of the periodic table.

These elements are situated in between s- and p-block elements and, therefore, their properties are also intermediate in between these two classes of elements. Hence, these are called as transitional elements. The properties of these elements are basically due to the presence of vacant or partially filled d-orbitals. The elements of zinc group have completely filled d-orbitals and, therefore, they do not show the common properties of these elements.

#### Different Transition Series and Electronic Configuration

**1. Electronic configuration :** They have similar electronic configuration. In the atoms of these elements d-subshell of the penultimate orbit is regularly filled. The electronic configurations of four transition series are given below :

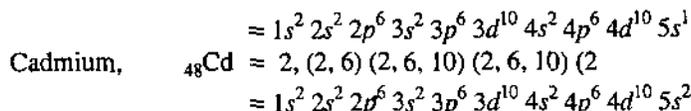
##### First Transition Series

Scandium, $_{21}\text{Sc}$	$= 2, (2, 6) (2, 6, 1) (2, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2)$
Titanium, $_{22}\text{Ti}$	$= 2, (2, 6) (2, 6, 2) (2, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2)$
Vanadium, $_{23}\text{V}$	$= 2, (2, 6) (2, 6, 3) (2, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2)$
Chromium, $_{24}\text{Cr}$	$= 2, (2, 6) (2, 6, 5) (1, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1)$
Manganese, $_{25}\text{Mn}$	$= 2, (2, 6) (2, 6, 5) (2, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2)$
Iron, $_{26}\text{Fe}$	$= 2, (2, 6) (2, 6, 6) (2, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2)$
Cobalt, $_{27}\text{Co}$	$= 2, (2, 6) (2, 6, 7) (2, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2)$
Nickel, $_{28}\text{Ni}$	$= 2, (2, 6) (2, 6, 8) (2, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2)$
Copper, $_{29}\text{Cu}$	$= 2, (2, 6) (2, 6, 10) (1, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1)$
Zinc, $_{30}\text{Zn}$	$= 2, (2, 6) (2, 6, 10) (2, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2)$

The change in the electronic configuration in the case of chromium and copper is due to the stability associated with half completed and completed subshells. The stability is due to large exchange energy of atoms of these elements.

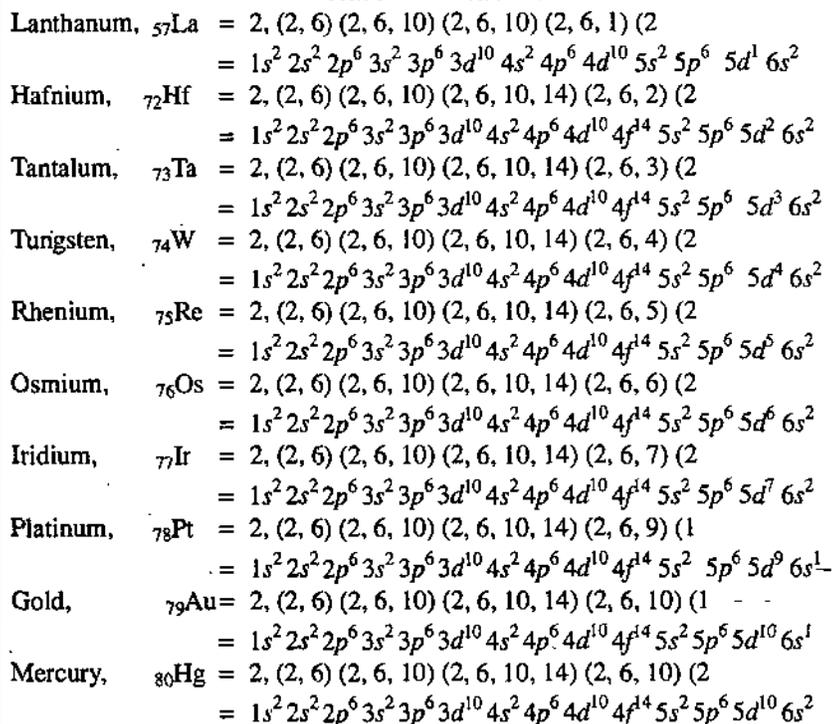
##### Second Transition Series

Yttrium, $_{39}\text{Y}$	$= 2, (2, 6) (2, 6, 10) (2, 6, 1) (2, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^1 5s^2)$
Zirconium, $_{40}\text{Zr}$	$= 2, (2, 6) (2, 6, 10) (2, 6, 2) (2, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^2 5s^2)$
Niobium, $_{41}\text{Nb}$	$= 2, (2, 6) (2, 6, 10) (2, 6, 4) (1, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^4 5s^1)$
Molybdenum, $_{42}\text{Mo}$	$= 2, (2, 6) (2, 6, 10) (2, 6, 5) (1, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5 5s^1)$
Technetium, $_{43}\text{Tc}$	$= 2, (2, 6) (2, 6, 10) (2, 6, 5) (2, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5 5s^2)$
Ruthenium, $_{44}\text{Ru}$	$= 2, (2, 6) (2, 6, 10) (2, 6, 7) (1, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^7 5s^1)$
Rhodium, $_{45}\text{Rh}$	$= 2, (2, 6) (2, 6, 10) (2, 6, 8) (1, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^8 5s^1)$
Palladium, $_{46}\text{Pd}$	$= 2, (2, 6) (2, 6, 10) (2, 6, 10) (0, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^0)$
Silver, $_{47}\text{Ag}$	$= 2, (2, 6) (2, 6, 10) (2, 6, 10) (1, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^1)$



The change in the electronic configurations in the case of molybdenum and silver is due to the stability associated with half completed and completed subshells. The anomalous electronic configuration of Nb, Ru, Rh and Pd is due to nuclear electronic attractions and interelectronic repulsions.

### Third Transition Series



### Fourth Transition Series



## • 6.2. GENERAL PROPERTIES OF ELEMENTS OF FIRST TRANSITION SERIES

### [I] General Properties of Transition Elements

(1) **Metallic character** : They are all metals because they have one or two electrons in the outermost shell which they can easily lose. These metals are ductile, malleable and are good conductors of heat and electricity. They form alloys with other metals. In the atoms of these elements both covalent and metallic bonding exist. Covalent bonding is responsible for hardness (mercury is an exception) and hardness increases with the increase in the number of unpaired *d*-electrons with the exception of manganese which seems to have a complex structure. Metallic bonding is responsible for their being good conductors of heat and electricity.

**(2) Atomic radii :** In general, the atomic radii of transition elements of a given series decrease as the atomic number increases but the decrease becomes small after midway. In the elements of first transition series, the atomic radii decrease slowly from scandium to chromium but from chromium to copper, these almost remains same. This is because in the elements of a given series, the number of shells remains the same but the nuclear charge increases. Moreover, the electrons entering in the  $d$ -subshell produce a screening effect which increases with the increase in the number of  $d$ -electrons. Thus, the two effects nuclear charge and screening effect oppose each other. In the midway both the effects, become nearly equal and thus; there is no change in the atomic radii. In the end of each transition series, the values of atomic radii are slightly higher. This is due to electron repulsion among  $d$ -electrons. These repulsions dominate at the end of each series and, therefore, size increases. For example, the atomic radii of elements of first transition series is given below :

First transition series	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radii	1.44Å	1.32Å	1.22Å	1.18Å	1.17Å	1.17Å	1.16Å	1.15Å	1.17Å	1.25Å

**(3) Atomic volume and density :** The atomic volume of transition elements is relatively less than  $s$  and  $p$ -block elements. This is because in these elements, the electrons are filled in the inner  $d$ -suborbitals and the nuclear charge increases. The atomic volume, therefore, decreases. As a result of decrease in volume, there is corresponding increase in density. Thus, the densities of these elements are quite high.

**(4) Melting and boiling points :** Except the elements of zinc group, the melting and boiling points of these elements are high. This is due to the stronger forces that bind their atoms together. The presence of one or more unpaired  $d$ -electrons is responsible for these forces on account of covalent bonding in them. Thus, their melting and boiling points increase with the increase in the number of unpaired  $d$ -electrons with the exception of manganese which seems to have a complex structure. Tungsten has highest melting point (3410°C) amongst transition elements.

The atoms of zinc group elements have completely filled  $d$ -orbitals. They, therefore, cannot form covalent bonds. Hence, the melting and boiling points of these elements are also less.

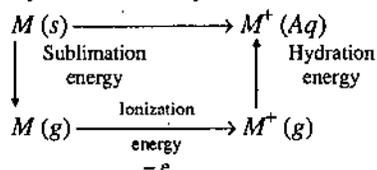
**(5) Ionization potentials :** The ionization potentials of these elements are in between  $s$ - and  $p$ -block elements. They have higher ionization potentials than  $s$ -block elements and lower than  $p$ -block elements. This indicates that these elements are less electropositive than  $s$ -block elements and are more electropositive than  $p$ -block elements.

In a given series of transition elements, the ionization potential slowly increases with the increase of atomic number. This is due to the increasing nuclear charge, but on the other hand,  $d$ -electrons provide a screening effect so that the effect of positive charge is reduced. Thus, due to both these factors, the ionization potential increases rather slowly in a given period.

The second ionization potentials of chromium ( $3d^5 4s^1$ ) and copper ( $3d^{10} 4s^1$ ) are much higher. This is because in these cases, the second electron is to be removed from the stable system.

**(6) Standard electrode potentials and stability of different oxidation states of transition metal ions in aqueous solutions :** The stability of a particular oxidation state in solution can be explained in terms of its electrode potential which, in turn, depends upon enthalpy of sublimation, ionization energy and hydration energy.

The process of conversion of solid metal in a particular oxidation state in aqueous solution can be represented by Born Haber cycle.



Thus, the conversion of  $M(s)$  into  $M^+(aq)$  involves the following three steps :

- (i)  $M(s) \longrightarrow M(g)$ ,  $\Delta H_1 =$  Enthalpy of sublimation
  - (ii)  $M(g) \longrightarrow M^+(g)$ ,  $\Delta H_2 =$  Ionization energy
  - (iii)  $M^+(g) + (aq) \longrightarrow M^+(aq)$ ,  $\Delta H_3 =$  Hydration energy
- $$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

The reaction  $M(s) \longrightarrow M^+(aq) + e$  will be spontaneous only when  $\Delta H$  is negative. Thus, more negative is the value of total energy change,  $\Delta H$  for a particular oxidation state in aqueous solution, greater will be the stability of that oxidation state. The electrode potential is a measure of

total energy change,  $\Delta H$ . The standard electrode potentials ( $E^\circ$ ) for  $\frac{M^{2+}}{M}$  for the elements of first transition series are given below :

Element	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$E^\circ \left( \frac{M^{2+}}{M} (aq) \right)$ in volts	-1.63	-1.20	-0.91	-1.18	-0.44	-0.28	-0.24	+0.34	-0.76

It is evident that there is no regular trend in these values. This is due to the fact that sublimation energies and ionization energies of the metals show irregular variation.

**(7) Reactivity :** These elements are chemically less reactive. This is due to their high heat of sublimation, high ionization energy and less hydration energy of their ions.

**(8) Oxidation states :** Except the elements of zinc group, they show variable oxidation states. This is because there is very little difference in the energy of outermost  $s$ - and the penultimate  $d$ -subenergy levels and electrons from both the energy levels may be used for bond formation. The different oxidation states of the elements of first transition series are given in the following table. The less common and unstable oxidation states are given in the brackets.

Element	Electronic configuration of outermost shell	Oxidation states						
	$3d$	$4s$						
$_{21}\text{Sc}$	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑</td><td></td><td></td><td></td><td></td></tr></table>	↑					<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑↓</td></tr></table> +2, +3	↑↓
↑								
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$_{22}\text{Ti}$	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑</td><td>↑</td><td></td><td></td><td></td></tr></table>	↑	↑				<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑↓</td></tr></table> (+2), +3, +4	↑↓
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$_{23}\text{V}$	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑</td><td>↑</td><td>↑</td><td></td><td></td></tr></table>	↑	↑	↑			<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑↓</td></tr></table> +2, +3, +4, +5	↑↓
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$_{24}\text{Cr}$	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑</td><td>↑</td><td>↑</td><td>↑</td><td>↑</td></tr></table>	↑	↑	↑	↑	↑	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑</td></tr></table> (+1), +2, +3, (+4), (+5), +6	↑
↑	↑	↑	↑	↑				
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$_{25}\text{Mn}$	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑</td><td>↑</td><td>↑</td><td>↑</td><td>↑</td></tr></table>	↑	↑	↑	↑	↑	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑↓</td></tr></table> +2, +3, +4, (+5), +6, +7	↑↓
↑	↑	↑	↑	↑				
↑↓								
$_{26}\text{Fe}$	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑↓</td><td>↑</td><td>↑</td><td>↑</td><td>↑</td></tr></table>	↑↓	↑	↑	↑	↑	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑↓</td></tr></table> +2, +3, (+4), (+5), (+6)	↑↓
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↑↓								
$_{27}\text{Co}$	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑↓</td><td>↑↓</td><td>↑</td><td>↑</td><td>↑</td></tr></table>	↑↓	↑↓	↑	↑	↑	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑↓</td></tr></table> +2, +3, (+4)	↑↓
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$_{28}\text{Ni}$	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑</td><td>↑</td></tr></table>	↑↓	↑↓	↑↓	↑	↑	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑↓</td></tr></table> +2, +3, +4	↑↓
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$_{29}\text{Cu}$	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑↓</td></tr></table>	↑↓	↑↓	↑↓	↑↓	↑↓	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑</td></tr></table> +1, +2	↑
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$_{30}\text{Zn}$	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑↓</td></tr></table>	↑↓	↑↓	↑↓	↑↓	↑↓	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>↑↓</td></tr></table> +2	↑↓
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From the above table it is observed that in the first five elements of first transition series upto Mn, the minimum oxidation state is equal to the number of  $4s$  electrons and the maximum oxidation state is equal to the sum of  $4s$  and  $3d$  electrons. In the next elements from iron to zinc, the minimum oxidation state is equal to the number of  $4s$  electrons and the maximum oxidation state is not related to their electronic configuration. Some of the transition metals such as chromium, iron and nickel also show zero oxidation state in metal carbonyls like  $\text{Cr}(\text{CO})_6$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{Ni}(\text{CO})_4$ .

The relative stability of different oxidation states can be explained on the basis of stability of  $d^0$ ,  $d^5$  and  $d^{10}$  configurations. For example,  $\text{Ti}^{4+}$  ( $3d^0 4s^0$ ) is more stable than  $\text{Ti}^{3+}$  ( $3d^1 4s^0$ ). Similarly,  $\text{Fe}^{3+}$  ( $3d^5 4s^0$ ) is more stable than  $\text{Fe}^{2+}$  ( $3d^6 4s^0$ ).

**(9) Formation of coloured salts :** These elements form coloured salts in the solid or in the solution state. The phenomenon of colour is associated with incomplete  $d$ -electron shells and excitation of electrons from the  $d$ -orbitals of lower energy to the  $d$ -orbitals of higher energy. The amount of energy required for  $d-d$  electron transitions is very small and is absorbed from the visible region. The rest of the light is, therefore, no longer white. The colours and outer electronic configurations of some of the ions of the elements of the first transition series are given in the table below. It has been observed that the transition metal ions having completely filled  $d$ -orbitals such as  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Au}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$  are all colourless as the excitation of electrons is not possible

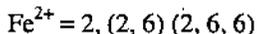
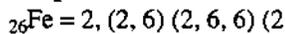
within *d*-orbitals. The transition metal ions having empty *d*-orbitals i.e.,  $\text{Sc}^{3+}$ ,  $\text{Ti}^{4+}$  are also colourless.

**Table : Colours and outer configuration of some of the ions of first transition series.**

Transition metal ion	Outer configuration	Colour
$\text{Sc}^{3+}$	$3d^0$	Colourless
$\text{Ti}^{3+}$	$3d^1$	Purple
$\text{Ti}^{4+}$	$3d^0$	Colourless
$\text{V}^{3+}$	$3d^2$	Green
$\text{V}^{5+}$	$3d^0$	Colourless
$\text{Cr}^{3+}$	$3d^3$	Violet
$\text{Mn}^{2+}$	$3d^5$	Light pink
$\text{Fe}^{2+}$	$3d^6$	Green
$\text{Fe}^{3+}$	$3d^5$	Yellow
$\text{Co}^{2+}$	$3d^7$	Pink
$\text{Ni}^{2+}$	$3d^8$	Green
$\text{Cu}^+$	$3d^{10}$	Colourless
$\text{Cu}^{2+}$	$3d^9$	Blue
$\text{Zn}^{2+}$	$3d^{10}$	Colourless

**(10) Formation of complex salts :** They form complex salts. This is due to the presence of small highly charged ions with vacant orbitals to accept lone pair of electrons donated by other atoms or groups. These atoms or groups are called as ligands and number of coordinate bonds formed by these ligands is called as coordination number of transition metal ion.

**(i) Complex compounds of iron**

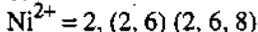
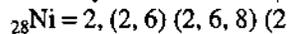


Formation of  $[\text{Fe}(\text{CN})_6]^{4-}$  complex ion by the gain of six electron pairs from six  $\text{CN}^-$  ions by  $\text{Fe}^{2+}$  ions.



$d^2 sp^3$  hybridization-octahedral structure-diamagnetic

**(ii) Complex compounds of nickel**

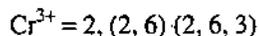
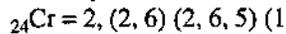


Formation of  $[\text{Ni}(\text{CN})_4]^{2-}$  complex ion by the gain of four electron pairs from four  $\text{CN}^-$  ions by  $\text{Ni}^{2+}$  ions.

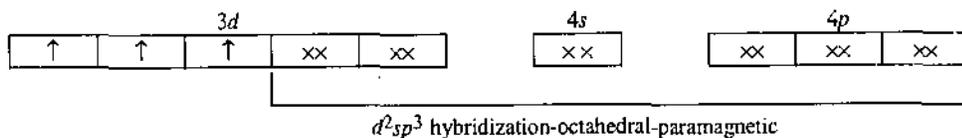


$dsp^2$  hybridization-square planar-diamagnetic

**(iii) Complex compounds of chromium**



Formation of  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  complex ion by gain of six electron pairs from six  $\text{NH}_3$  molecules by  $\text{Cr}^{3+}$  ions.



**(11) Magnetic properties :** Except the elements of zinc group they are paramagnetic, *i.e.*, they are attracted into the magnetic field. This is due to the presence of unpaired electrons in the  $(n-1)$   $d$ -orbitals. The elements of zinc group are, however, diamagnetic, *i.e.*, they are repelled by the magnetic field. This is due to the absence of unpaired electrons. Iron, cobalt and nickel are ferromagnetic as their paramagnetic character is much more than others. The paramagnetic substance weighs more whereas a diamagnetic substance weighs less in a magnetic field.

The electrons determine the magnetic properties in two ways:

(i) Each electron behaves as a tiny magnet spinning about its own axis. The spinning of the charge produces a magnetic moment known as spin magnetic moment of the electron.

(ii) The moving electron in an orbit also produces a magnetic moment known as orbital moment.

Thus, the magnetic properties of an atom, ion or molecule result from the combination of spin magnetic moment and orbital magnetic moment. The magnetic moment is generally expressed in the units called Bohr magnetons (B.M.)

$$1 \text{ B.M.} = \frac{eh}{4\pi mc}$$

where  $e$  = charge of the electron in e.s.u.

$h$  = Planck's constant

$m$  = mass of the electron.

$c$  = velocity of light.

**(a) Spin magnetic moment of a single unpaired electron :** The spin magnetic moment  $\mu_s$  of a single unpaired electron is given by wave mechanics as

$$\mu_s \text{ (in B.M.)} = g \sqrt{s(s+1)} \quad \dots (i)$$

where  $s$  = spin quantum number

$g$  = gyromagnetic ratio.

For a free electron, the value of  $g = 2$  and  $s = \frac{1}{2}$ , the spin magnetic moment  $\mu_s$  for a single unpaired electron is given by,

$$\begin{aligned} \mu_s &= 2 \sqrt{\frac{1}{2} \left( \frac{1}{2} + 1 \right)} \\ &= 2 \sqrt{\frac{1}{2} \times \frac{3}{2}} = \sqrt{2} = 1.73 \text{ B.M.} \end{aligned}$$

**(b) Spin magnetic moment for an atom, ion or molecule containing more than one unpaired electron :** If the total spin quantum number for  $n$  unpaired electrons is  $S$ , then the spin magnetic moment  $\mu_s$  is given by

$$\mu_s = 2 \sqrt{S(S+1)}$$

where  $S$  = Number of unpaired electrons  $\times$  spin quantum number of a single electron.

$$n \times \frac{1}{2} = \frac{n}{2}$$

Putting  $S = \frac{n}{2}$ , we have

$$\begin{aligned} \mu_s &= 2 \sqrt{\frac{n}{2} \left( \frac{n}{2} + 1 \right)} \\ &= 2 \sqrt{\frac{n}{2} \left( \frac{n+2}{2} \right)} = \sqrt{n(n+2)} \quad \dots (ii) \end{aligned}$$

The above equation shows that the spin magnetic moment  $\mu_s$  is directly related to the number of unpaired electrons. The spin magnetic moment for various numbers of unpaired electrons may be calculated as

when	$n = 1$ (e.g., $Ti^{3+}$ ) $\mu_s = \sqrt{1(1+2)} = \sqrt{3} = 1.73$ B.M.
when	$n = 2$ (e.g., $V^{3+}$ ) $\mu_s = \sqrt{2(2+2)} = \sqrt{8} = 2.83$ B.M.
when	$n = 3$ (e.g., $Cr^{3+}$ ) $\mu_s = \sqrt{3(3+2)} + \sqrt{15} = 3.87$ B.M.
when	$n = 4$ (e.g., $Fe^{2+}$ ) $\mu_s = \sqrt{4(4+2)} = \sqrt{24} = 4.90$ B.M.
when	$n = 5$ (e.g., $Mn^{2+}$ ) $\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.92$ B.M.

However, the experimental value of magnetic moments is generally higher from the spin only values. This is because the orbital motion of the electrons also makes a contribution to the magnetic moment. The magnetic moment for ions whose orbital angular momentum makes its full contribution to the magnetic moment is given by

$$\mu_{s+L} = \sqrt{4S(S+1) + L(L+1)} \text{ B.M.}$$

where  $L$  is the resultant orbital angular quantum number.

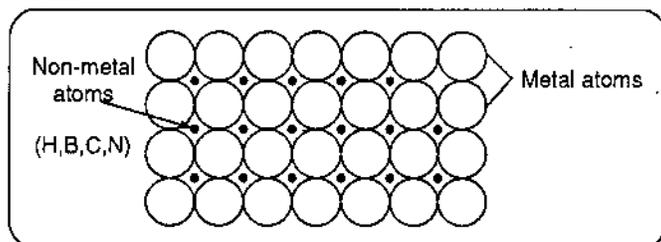
It is observed that the actual magnetic moments are higher than  $\mu_s$  but are not as high as  $\mu_{s+L}$ . This is because the electric fields of other atoms, ions and molecules surrounding the central metal ion in the complexes restrict the orbital motion of the electrons. As a result, the orbital moments decrease.

**(12) Catalytic properties :** Most of the transition metals and their compounds possess catalytic activity. Iron, chromium, nickel, platinum etc. metals are used as catalysts in different chemical reactions. The transition elements on account of their variable valency can form unstable intermediate compounds which readily decompose to give the product and the catalyst is regenerated. They also offer a large surface area for the reactants to be adsorbed so that the products are readily obtained.

**(13) Formation of non-stoichiometric compounds :** The transition elements on account of their variable valency can form non-stoichiometric compounds, i.e., compounds of indefinite proportion. These compounds do not follow the general valency rules. For example, in ferrous oxide ( $FeO$ ) the ratio of iron and oxygen is not 1 : 1, but it varies from  $Fe_{0.94}O$  to  $Fe_{0.84}O$ . Therefore, it is a non-stoichiometric compound. Similarly, vanadium and selenium also form non-stoichiometric compounds  $VSe_{0.98}$ ,  $VSe_{1.2}$  etc.

**(14) Formation of interstitial compounds :** The transition metals form interstitial compounds with small non-metal atoms such as H, B, C and N.

In these compounds, non-metal atoms penetrate into the crystal lattice of transition metal with the result that the crystal lattice gets slightly distorted. These compounds resemble the parent transition metal in chemical properties but differ in some physical properties like density, hardness and conductivity etc. For example, steel and cast iron are hard because of the formation of interstitial compounds with carbon.



**(15) Alloy formation :** The atomic size of the transition metals is very similar and hence in the crystal lattice one metal can be readily replaced by another metal giving alloys. The alloys so formed are hard and have high melting points.

## 6.3. COMPARATIVE STUDY OF ELEMENTS OF SECOND AND THIRD TRANSITION SERIES

**(i) Atomic radii :** In general, the atomic radii of transition elements of a given series decrease as the atomic number increases but decrease becomes small after midway and then it increases

towards the end of the series. Similar behaviour has been observed in the elements of second and third transition series. The atomic radii of these elements are given in the following table :

First transition series	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radii	1.44Å	1.32Å	1.22Å	1.18Å	1.17Å	1.17Å	1.16Å	1.15Å	1.17Å	1.25Å
Second transition series	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Atomic radii	1.62Å	1.45Å	1.34Å	1.29Å	—	1.25Å	1.25Å	1.28Å	1.34Å	1.48Å
Third transition series	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Atomic radii	1.69Å	1.44Å	1.34Å	1.30Å	1.28Å	1.26Å	1.26Å	1.29Å	1.34Å	1.49Å

In general, atomic radii increase while going down the group. Therefore, the atomic radii of the elements of second transition series have higher values than those of the elements of first transition series. This is due to increase in the number of electron shells. The atomic radii of the elements of third transition series except lanthanum have almost the same atomic radii as the elements of second transition series. This is due to lanthanide contraction. The fourteen lanthanides are present between lanthanum and hafnium ( $_{57}\text{La} - _{72}\text{Hf}$ ) and there is a continuous decrease in atomic size from cerium ( $_{58}\text{Ce}$ ) to lutecium ( $_{71}\text{Lu}$ ) so that the atomic size of hafnium becomes almost equal to the size of zirconium.

(ii) **Ionic radii** : The ionic radii also follow the same trend. Since the transition metals have different oxidation states, the radii of the ions also differ. In a given transition series, for the same oxidation state ionic radii generally decrease as the atomic number increases. For example, in the first transition series, the radii of bivalent metal ions is given below :

Ion ( $M^{2+}$ )	$\text{Sc}^{2+}$	$\text{Ti}^{2+}$	$\text{V}^{2+}$	$\text{Cr}^{2+}$	$\text{Mn}^{2+}$	$\text{Fe}^{2+}$	$\text{Co}^{2+}$	$\text{Ni}^{2+}$	$\text{Cu}^{2+}$
Ionic radii	0.95Å	0.90Å	0.88Å	0.84Å	0.80Å	0.76Å	0.74Å	0.72Å	0.69Å

The ionic radii decrease with increase in oxidation state.

$$\text{Sc}^{2+} = 0.95\text{Å} \quad \text{Ti}^{2+} = 0.90\text{Å} \quad \text{Fe}^{2+} = 0.76\text{Å}$$

$$\text{Sc}^{3+} = 0.81\text{Å} \quad \text{Ti}^{3+} = 0.76\text{Å} \quad \text{Fe}^{3+} = 0.64\text{Å}$$

(iii) **Ionization potential** : The ionization potential of these elements is in between *s*- and *p*-block elements. They have higher ionization potential than *s*-block elements and lower than *p*-block elements. This indicates that these elements are less electropositive than *s*-block elements and are more electropositive than *p*-block elements.

In a given series of transition elements, the ionization potential slowly increases with the increase of atomic number. This is due to the increasing nuclear charge but on the other hand, *d*-electrons provide a screening effect so that the effect of positive charge is reduced. Thus, due to both these factors, the ionization potential increases rather slowly in a given period.

The second ionization potential of chromium ( $3d^5 4s^1$ ) and copper ( $3d^{10} 4s^1$ ) is much higher. This is because in these cases, the second electron is to be removed from the stable system.

In general, ionization potential decreases while going down the group. Therefore, ionization potential of the elements of second transition series has lower values than those of the elements of first transition series as expected. However, ionization potential of the elements of third transition series except lanthanum has higher value of ionization potential due to lanthanide contraction. The atomic radii of the elements of second and third transition series are almost same but atomic numbers differ by 32. Thus, the outer electrons are firmly attached to the nucleus and ionization potential values are very high. On account of this, the elements of third transition series are almost inert under ordinary conditions.

(iv) **Oxidation state** : Except few elements, they show variable oxidation state. This is because there is very little difference in the energies of outermost *s*- and penultimate *d*- subenergy levels and electrons from both the energy levels may be used for bond formation. The different oxidation states of transition elements are given in the following table. The less common and unstable oxidation states are given in brackets :

First Transition Series		Second Transition Series		Third Transition Series	
Element	Different oxidation states	Element	Different oxidation states	Element	Different oxidation states
Sc	+2, +3	Y	+3	La	+3
Ti	(+2), +3, +4	Zr	+3, +4	Hf	(+3), +4
V	+2, +3, +4, +5	Nb	(+2), (+3), (+4), +5	Ta	(+2), (+3), (+4), +5
Cr	(+1), +2, +3, (+4), (+5), +6	Mo	(+2), +3, +4, +5, +6	W	+2, (+3), +4, +5, +6
Mn	+2, +3, +4, (+5), +6, +7	Tc	(+4), (+5), +7	Re	+3, +4, (+5), (+6), +7
Fe	+2, +3, (+4), (+5), (+6)	Ru	+2, +3, +4, (+5), (+6), (+7), (+8)	Os	+2, +3, +4, +6, +8
Co	+2, +3, (+4)	Rh	+2, +3, +4, (+6)	Ir	+2, +3, +4, (+6)
Ni	+2, +3, +4	Pd	+2, (+3), +4	Pt	+2, (+3), +4, (+5), (+6)
Cu	+1, +2	Ag	+1, (+2), (+3)	Au	+1, +3
Zn	+2	Cd	+2	Hg	+1, +2

The stability of a given oxidation state depends upon the nature of the element with which transition metal combines. The highest oxidation state is found in the compounds of fluorine and oxygen. This is due to small size and high electronegativity of these elements.

From the above table, it is observed that :

(i) The minimum oxidation state is equal to the number of  $ns$  electrons. For example, in the elements of first transition series, the lowest oxidation state of chromium ( $3d^5 4s^1$ ) and copper ( $3d^{10} 4s^1$ ) is +1 while for others ( $3d^{1-10} 4s^2$ ) it is +2.

(ii) For the first five elements of a transition series, the minimum oxidation state is equal to the number of  $ns$  electrons and other oxidation states are given by the sum of outer  $s$  and some or all  $d$ -electrons. The highest oxidation state is equal to the sum of  $ns$  and  $(n-1)$   $d$  electrons. In the case of remaining five elements, the minimum oxidation state is given by the number of  $ns$  electrons while the maximum oxidation state is not related to their electronic configurations.

(iii) Some of the transition metals such as chromium, iron and nickel also show zero oxidation state in metal carbonyls like  $\text{Cr}(\text{CO})_6$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{Ni}(\text{CO})_4$ .

(iv) The highest oxidation state shown by any transition metal is +8. For example, ruthenium and osmium show +8 oxidation state in some of their compounds.

(v) Except scandium, the most common oxidation state of the elements of first transition series is +2 which arises due to the loss of two  $4s$  electrons. This indicates that after scandium  $d$ -orbitals become more stable than the  $s$ -orbital.

(vi) The transition elements in lower oxidation state (+2 and +3) generally form ionic compounds whereas in higher oxidation states, the bonds formed are covalent.

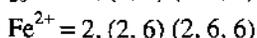
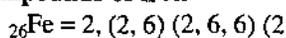
(vii) In each group, the highest oxidation state increases with atomic number. For example, in group VIII, the common oxidation states of iron are +2 and +3 but ruthenium and osmium in the same group show oxidation states +4, +6 and +8.

(viii) The relative stability of different oxidation states can be explained on the basis of stability of  $d^0$ ,  $d^5$  and  $d^{10}$  configurations. For example,  $\text{Ti}^{4+}$  ( $3d^0 4s^0$ ) is more stable than  $\text{Ti}^{3+}$  ( $3d^1 4s^0$ ). Similarly,  $\text{Fe}^{3+}$  ( $3d^5 4s^0$ ) is more stable than  $\text{Fe}^{2+}$  ( $3d^6 4s^0$ ).

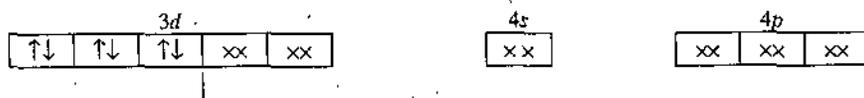
(ix) In  $3d$ -series lower oxidation states, i.e., +2 and +3 are most stable whereas in  $4d$  and  $5d$ -series higher oxidation states, i.e., +5 to +8 are most stable.

(v) **Complex Formation** : They form complex salts. This is due to the presence of small highly charged ions with vacant orbitals to accept lone pair of electrons donated by other atoms or groups. These atoms or groups are called ligands and number of coordinate bonds formed by these ligands is called coordination number of transition metal ion.

#### Complex compounds of iron

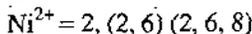
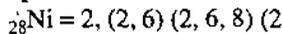


Formation of  $[\text{Fe}(\text{CN})_6]^{4-}$  complex ion by the gain of six electron pairs from six  $\text{CN}^-$  ions by  $\text{Fe}^{2+}$  ions.

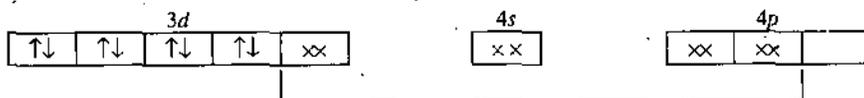


$d^2sp^3$  hybridization octahedral structure-diamagnetic

**Complex compounds of nickel**

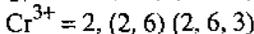
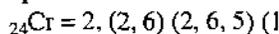


Formation of  $[\text{Ni}(\text{CN})_4]^{2-}$  complex ion by the gain of four electron pairs from four  $\text{CN}^-$  ions by  $\text{Ni}^{2+}$  ions.



$dsp^2$  hybridization-square planar-diamagnetic

**Complex compounds of chromium**

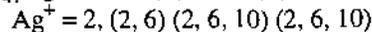
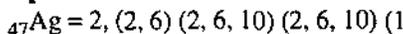


Formation of  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  complex ion by gain of six electron pairs from six  $\text{NH}_3$  molecules by  $\text{Cr}^{3+}$  ions.

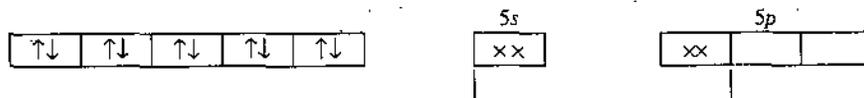


$d^2sp^3$  hybridization-octahedral-paramagnetic

**Complex compounds of silver**



Formation of  $[\text{Ag}(\text{NH}_3)_2]^+$  complex ion by gain of two electron pairs from two  $\text{NH}_3$  molecules by  $\text{Ag}^+$  ions.



$sp$ -hybridization-linear-diamagnetic

**Trends in Different Transition Series for Complex Formation**

- (1) In a given transition series and for a given oxidation state, the stability of the complex increases as the atomic number increases.
- (2) If the transition metal shows more than one oxidation state, the transition metal ion with higher oxidation state forms more stable complex.
- (3) The elements of first transition series form stable complexes with N, O, F donor ligands whereas the elements of second and third transition series form stable complexes with P, S and halogen donor ligands.

**• 6.4. EXPLANATION OF FACTS WITH REASON**

**(1) Transition elements are called d-block elements.**

The transitional elements are characterised by the regular filling of  $d$ -subenergy level of their electronic configuration, therefore, these are called  $d$ -block elements. In these elements, there is a regular filling of  $3d$ ,  $4d$ ,  $5d$  or  $6d$ -subenergy levels and, therefore, these elements have four series.

**(2) Transition elements are not found in the lithium and sodium periods.**

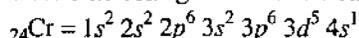
Transitional elements are characterized by the regular filling of  $d$ -subenergy levels of their electronic configuration. Lithium and sodium belong to the second and third periods of the periodic table. There are no transition elements in these periods because there are no  $d$ -orbitals available for the filling of electrons.

**(3) Zinc and cadmium are normally not considered as transition metals.**

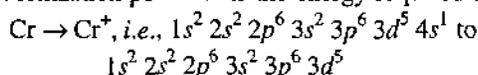
Transition elements are the elements whose atoms or simple ions contain partially filled  $d$ -orbitals. Zn and Cd are normally not considered as transition metals as they contain completely filled  $d$ -orbitals in their elementary and commonly occurring ions.

**(4) The second ionization potential of chromium is very high.**

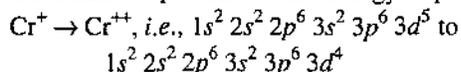
The electronic configuration of chromium is



First ionization potential is the energy required to convert



Second ionization potential is the energy required to convert



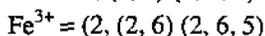
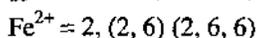
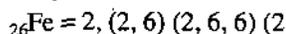
The second ionization potential of chromium is very high as compared to its first ionization potential because after the removal of outer electron the effective nuclear charge is increased and the removal of the second electron will have to be done against greater nuclear attractions. Secondly, the second electron is to be removed from the half completed subshell, *i.e.*, from the stable system. Therefore, the amount of energy required for the said removal will be very high.

**(5) Transition metals are chemically less reactive.**

The transition metals are chemically less reactive. This is due to their high heat of sublimation, high ionization energy and less hydration energy of their ions.

**(6) Transition metals show variable valency.**

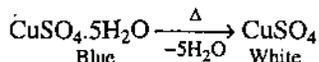
The transition metals show variable valency. This is because there is a very little difference in the energy of outermost  $s$ - and the penultimate  $d$ -sub energy levels and electrons from both the energy levels may be used for bond formation.

**(7)  $\text{Fe}^{3+}$  ion is more stable than  $\text{Fe}^{2+}$  ion.**

The electronic configuration of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  indicates that  $\text{Fe}^{3+}$  ion has half completed  $d$ -subshell. Hence,  $\text{Fe}^{3+}$  ion is more stable than  $\text{Fe}^{2+}$  ion.

**(8) Anhydrous copper sulphate is white but hydrated copper sulphate is blue.**

Anhydrous copper sulphate is white but hydrated copper sulphate is blue. This is because in the hydrated form it contains hydrated ions,  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  which are blue.

**(9)  $\text{Zn}^{2+}$  salts are white while  $\text{Cu}^{2+}$  salts are blue.**

$\text{Zn}^{2+}$  salts are white while  $\text{Cu}^{2+}$  salts are blue. The colour of the transition metal ions is due to incomplete  $d$ -electron shells and excitation of electrons from  $d$ -orbitals of lower energy to  $d$ -orbitals of higher energy. The amount of energy required for this  $d$ - $d$  electron transition is very small and is absorbed from the visible region. The rest of the light is, therefore, no longer white.

In the case of  $\text{Zn}^{2+}$  ions,  $d$ -orbitals are completely filled. Hence,  $d$ - $d$  electron transition is not possible. They do not absorb any radiation from the visible region and, therefore,  $\text{Zn}^{2+}$  salts are white. In the  $\text{Cu}^{2+}$  salts ( $d^9$  configuration) one of the  $d$ -orbitals is partially filled. Hence, transition of electron can take place from the  $d$ -orbitals of lower energy to the  $d$ -orbitals of higher energy.  $\text{Cu}^{2+}$  salts absorb red light for this  $d$ - $d$  electron transition and, therefore, appear blue.

**(10)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is coloured while  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  is colourless.**

$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is coloured while  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  is colourless. The colour of these complex ions is due to incomplete  $d$ -electron shells and excitation of electrons from the  $d$ -orbitals of lower energy to the  $d$ -orbitals of higher energy. The amount of energy required for this  $d-d$  electron transitions is very small and is absorbed from the visible region. The rest of the light is, therefore, no longer white.

$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  complex ion has one electron in the  $d$ -subshell. Hence, transition of electron can take place from the  $d$ -orbital of lower energy to the  $d$ -orbital of higher energy. This complex ion absorbs yellow light for this  $d-d$  electron transition and, therefore, appears purple. In the  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  complex ion,  $d$ -orbitals are vacant and hence  $d-d$  electron transition is not possible. Therefore, this complex ion is colourless.

**(11) Transition metals form complex salts.**

The transition metals form complex salts. This is due to the presence of small highly charged ions with vacant orbitals to accept lone pair of electrons donated by other atoms or groups. These atoms or groups are called ligands and number of coordinate bonds formed by these ligands is called coordination number of transition metal ion. For example, iron forms a complex  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , nickel forms a complex  $\text{K}_2[\text{Ni}(\text{CN})_4]$  etc.

**(12) Transition metals are paramagnetic**

The transition metals are paramagnetic, i.e., they are attracted into the magnetic field. This is due to the presence of unpaired electrons in the  $(n-1)d$  orbitals.

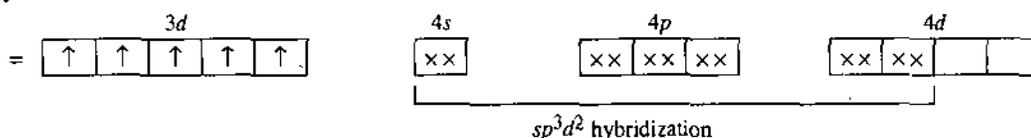
**(13)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  ion is more paramagnetic, than  $[\text{Fe}(\text{CN})_6]^{3-}$  ion.**

We have  ${}_{26}\text{Fe} = 2, (2, 6) (2, 6, 6) (2)$

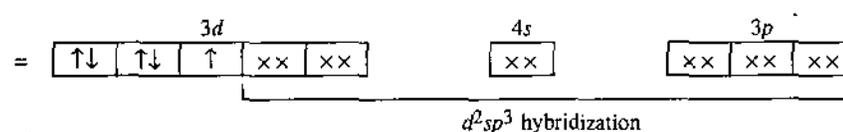
$\text{Fe}^{3+} = 2, (2, 6) (2, 6, 5)$



Formation of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  complex ion by gain of six electron pairs from six  $\text{H}_2\text{O}$  molecules by  $\text{Fe}^{3+}$  ions.



Formation of  $[\text{Fe}(\text{CN})_6]^{3-}$  complex ion by gain of six electron pairs from six  $\text{CN}^-$  ions by  $\text{Fe}^{3+}$  ions.



There are five unpaired electrons in the electronic structure of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  ion and one unpaired electron in the electronic structure of  $[\text{Fe}(\text{CN})_6]^{3-}$  ion. Since paramagnetic character depends upon the number of unpaired electrons,  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  ion is more paramagnetic than  $[\text{Fe}(\text{CN})_6]^{3-}$  ion.

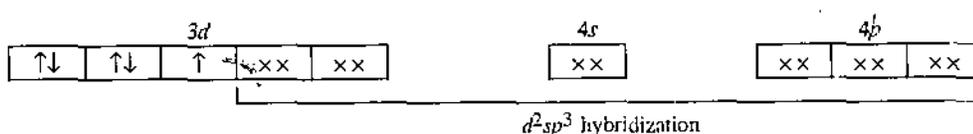
**(14)  $[\text{Fe}(\text{CN})_6]^{3-}$  ion is weakly paramagnetic while  $[\text{Fe}(\text{CN})_6]^{4-}$  ion is diamagnetic.**

${}_{26}\text{Fe} = 2, (2, 6) (2, 6, 6) (2)$

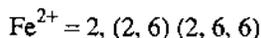
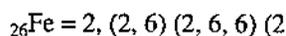
$\text{Fe}^{3+} = 2, (2, 6) (2, 6, 5)$



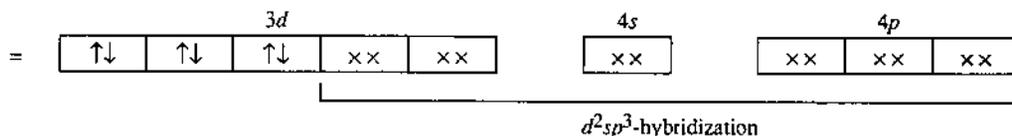
Formation of  $[\text{Fe}(\text{CN})_6]^{3-}$  complex ion by gain of six electron pairs from six  $\text{CN}^-$  ions by  $\text{Fe}^{3+}$  ions.



Due to the presence of one unpaired electron in  $[\text{Fe}(\text{CN})_6]^{3-}$  ion, it is weakly paramagnetic.



Formation of  $[\text{Fe}(\text{CN})_6]^{4-}$  complex ion by gain of six electron pairs from six  $\text{CN}^-$  ions by  $\text{Fe}^{2+}$  ions.



Due to the presence of all paired electrons  $[\text{Fe}(\text{CN})_6]^{4-}$  ion is diamagnetic.

**(15) Transition metals form alloys with other transition metals easily.**

Transition metals form alloys with other transition metals easily. This is because the atomic size of the transition metals is very much similar and hence in the crystal lattice one metal can be easily replaced by another metal giving alloys.

**(16) Atomic radii of second and third series of transition elements are almost equal.**

The atomic radii of second and third series of transition elements are almost equal due to lanthanide contraction :

First Transition Series	21Sc	22Ti	23V	24Cr
Atomic radii	1.44Å	1.32Å	1.22Å	1.18Å
Second Transition Series	39Y	40Zr	41Nb	42Mo
Atomic radii	1.62Å	1.45Å	1.34Å	1.29Å
Third Transition Series	57La	72Hf	73Ta	74W
Atomic radii	1.69Å	1.44Å	1.34Å	1.30Å

The fourteen lanthanides are present between lanthanum and hafnium ( ${}_{57}\text{La} - {}_{72}\text{Hf}$ ) and there is a continuous decrease in size from cerium ( ${}_{58}\text{Ce}$ ) to lutecium ( ${}_{71}\text{Lu}$ ) so that the atomic size of hafnium becomes almost equal to the size of zirconium.

**(17) Ionization energies of 5d elements are greater than those of 3d elements.**

Ionization energies of 5d elements (third transition series) are greater than those of 3d elements (first transition series) due to lanthanide contraction.

First Transition Series (3d Series)	21Sc	22Ti	23V	24Cr
Second Transition Series (4d Series)	39Y	40Zr	41Nb	42Mo
Third Transition Series (5d Series)	57La	72Hf	73Ta	74W

The atomic radii of the elements of third transition (5d) series are slightly greater than those of first transition (3d) series but atomic numbers differs by 50. Thus, in the 5d series the outer electrons are firmly attached to the nucleus and ionization energies are very high.

**SUMMARY**

- Transition elements are elements with atoms in which the two outermost shells are incomplete, whereas all the rest shells are complete.
- The electronic configuration of the two outermost shells is  $(n-1)s^2, (n-1)p^6, (n-1)d^{1-9}, ns^{1-2}$ .
- Elements of groups I B, II B, ..... VII B and VIII are transition elements.
- There are four transition series.
- The elements of first transition series are chemically less reactive.
- The elements of first transition series form complex salts.
- The elements of second and third transition elements, except a few, show variable oxidation states.
- The elements of second and third transition series form complex salts.

• **STUDENT ACTIVITY**

1. What are transition elements ? Why are they so called ?

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2. Discuss the ionisation potentials and atomic radii of elements of first transition series.

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3. Compare the oxidation states and ionic radii of elements of second and third transition series.

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4. Why is anhydrous copper sulphate white, whereas hydrated salt is blue ?

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## • TEST YOURSELF

Answer the following questions :

- Explain why ionisation energies of 5d elements are greater than those of 3d elements.
- Explain why transition elements are paramagnetic in nature.
- Transition metals form alloys with other transition metals easily. Explain why.
- Why do transition metals form complex salts ?
- $\text{Zn}^{2+}$  salts are white, whereas  $\text{Cu}^{2+}$  salts are blue, explain with reason.
- Why is the second ionisation potential of chromium very high ?
- $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is coloured, whereas  $[\text{Se}(\text{H}_2\text{O})_6]^{3+}$  is colourless. Explain the fact with proper reasoning.
- Describe the general properties of transition elements of first transition series with respect to metallic character, atomic radii, ionisation potential.
- Mention the various series of transition elements by giving their electronic configuration.
- State and explain transition elements with examples.
- Discuss and compare the general properties of transition elements of second and third series with respect to :
  - Atomic radii
  - Ionic radii
  - Ionisation potential
  - Oxidation states
  - Complex formation
- The effective atomic number of Ni in Nickel carbonyl is :
  - 0
  - 4
  - 28
  - 36
- In transition elements, the incoming electron occupies  $(n-1)d$  sublevel in preference to :
  - $ns$
  - $np$
  - $(n-1)p$
  - $(n+1)s$
- The number of unpaired electrons in the ground state of Fe is :
  - 2
  - 4
  - 3
  - 5
- The colour of  $\text{Cu}_2\text{Cl}_2$  is :
  - Blue
  - Green
  - Black
  - White
- Which of the following ions shows highest magnetic moment ?
  - $\text{V}^{3+}$
  - $\text{Cr}^{3+}$
  - $\text{Fe}^{3+}$
  - $\text{Co}^{3+}$
- Which one of the given transition metal ions is diamagnetic ?
  - $\text{Co}^{2+}$
  - $\text{Ni}^{2+}$
  - $\text{Cu}^{2+}$
  - $\text{Zn}^{2+}$
- Which of the following has a unique electronic configuration ?
  - Cr
  - Pd
  - La
  - U
- Among the following ions which one has the highest paramagnetism?
  - $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
  - $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
  - $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$
  - $[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$
- The number of unpaired electrons in a complex compound is 2, the magnetic moment of the complex compound is :
  - 1.73
  - 2.45
  - 2.83
  - 3.87
- Which of the following complexes has the highest molar conductivity in solution ?
  - $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$
  - $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
  - $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
  - $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$
- Which of the following ions is coloured in solution ?
  - $\text{Cu}^+$
  - $\text{Zn}^{2+}$
  - $\text{V}^{3+}$
  - $\text{Ti}^{4+}$
- Which of the following has the maximum number of unpaired  $d$ -electrons ?
  - $\text{Mg}^{2+}$
  - $\text{Ti}^{3+}$
  - $\text{V}^{3+}$
  - $\text{Fe}^{3+}$
- The number of unpaired electrons in  $\text{Ni}^{2+}$  ( $Z = 28$ ) is :
  - 0
  - 2
  - 4
  - 8
- Which of the following ions does not give coloured solution ?
  - $\text{Cr}^{3+}$
  - $\text{Mn}^{2+}$
  - $\text{Fe}^{2+}$
  - $\text{Zn}^{2+}$
- Fill in the blanks :
  - The most abundant transition metal is .....
  - The outer electronic configuration of chromium is .....
  - The possible oxidation states of Titanium ( $Z = 22$ ) are .....
  - In transition elements, the differentiating electron enters in the ..... subenergy level.
  - The general electronic configuration of transition elements is .....

- (vi) The first transition element is .....
- (vii) The maximum number of unpaired electrons which a  $d$ -subshell can have is .....
- (viii) Most of the compounds of the transition metals are .....

**ANSWERS**

12. (iv); 13. (ii); 14. (ii); 15. (iv); 16. (iii); 17. (iv); 18. (ii); 19. (ii);  
20. (iii); 21. (i); 22. (iii); 23. (iv); 24. (ii); 25. (iv)..

26. Fill in the blanks :

(i) Iron (ii)  $3d^5 4s^1$  (iii) +2, +3, +4 (iv)  $d$   
(v)  $(n-1)s^2 (n-1)p^6 (n-1)d^{1-9} ns^{1-2}$  (vi) Scandium (vii) 5 (viii) coloured



## 7

## COORDINATION COMPOUNDS

## STRUCTURE

- Introduction
- Werner's Coordination Theory
- Sidwick Interpretation of Coordination Compounds
- IUPAC Nomenclature of Coordination Compounds
- Isomerism in Coordination Compounds
- Valency Bond Theory
- Inner and Outer Orbital Complexes
  - Summary
  - Student Activity
  - Test Yourself

## LEARNING OBJECTIVES

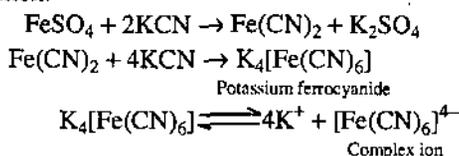
After going this unit you will learn :

- Complex salts, complex ion, ligand, coordination number and chelate compounds.
- Distinction between chelate and complex compounds.
- Werner's theory of coordination compounds.
- Electronic interpretation of Werner's theory of coordination compounds.
- Rules for naming the complex compounds.
- Structural and stereo isomerism
- Valency bond theory and its limitations.

## 7.1. INTRODUCTION

**[i] Complex Salts**

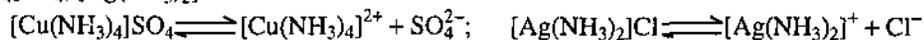
When two salt solutions combine together to form new compounds in which the constituent ions lose their identity, the resulting compounds are called complex salts. On ionization, they give complex ions in solution.



In the above compound, it is not possible to test for  $\text{Fe}^{2+}$  and  $\text{CN}^-$  ions but we can have a test for complex  $[\text{Fe}(\text{CN})_6]^{4-}$  ions.

These salts are generally of following three types :

**(i) Cationic complexes** : In these complexes, complex ion is cation. For example,  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ ,  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  etc.



**(ii) Anionic complexes** : In these complexes, complex ion is anion. For example,  $\text{K}_2[\text{Ni}(\text{CN})_4]$ ,  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$  etc.

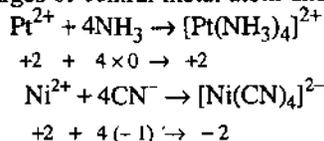


**(iii) Molecular complexes** : These complexes do not ionize in solution. For example,  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ ,  $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]$ ,  $[\text{Ni}(\text{CO})_4]$  etc.

**[ii] Complex Ion**

Complex ion is defined as an electrically charged ion formed by the combination of a central metal atom or ion and a suitable number of neutral molecules or anions. These neutral molecules

or anions are called ligands. For example, the complex compound  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  contains complex ion,  $[\text{Pt}(\text{NH}_3)_4]^{2+}$ . This ion is formed by the combination of  $\text{Pt}^{2+}$  ions and four  $\text{NH}_3$  molecules. Similarly, the complex compound  $\text{K}_2[\text{Ni}(\text{CN})_4]$  contains complex ion,  $[\text{Ni}(\text{CN})_4]^{2-}$ . This ion is formed by the combination of  $\text{Ni}^{2+}$  and four  $\text{CN}^-$  ions. The total charge on the complex ion is the resultant of the charges of central metal atom and ligands.



The complex ion carrying a positive charge is known as cationic complex and the complex ion carrying a negative charge is known as anionic complex. Some common examples are :

**Cationic complex :**  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ ,  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ .

**Anionic complex :**  $\text{K}_2[\text{Ni}(\text{CN})_4]$ ,  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ .

According to IUPAC system in naming complex ions, the ligands are named first followed by the name of central metal ion. If the complex ion is a cation, the central metal ion is named by its usual name. Thus,  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  is named as hexamine chromium (III) ion. If complex ion is anion, the name of the central metal ion is made to end in 'ate'. Thus,  $[\text{Ni}(\text{CN})_4]^{2-}$  is named as tetra cyano nickelate (II) ion.

### [III] Ligand

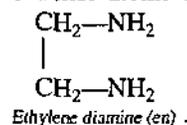
The neutral molecules or ions which surround the central metal atom or ion in a complex are called ligands. For example, in the complex ion,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $\text{Cu}^{2+}$  is central metal ion and  $\text{NH}_3$  molecules are ligands. Similarly, in the complex ion  $[\text{Ag}(\text{CN})_2]^-$ ,  $\text{Ag}^+$  is the central metal ion and  $\text{CN}^-$  ions are ligands.

The ligands are polar molecules such as  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CO}$  or anions such as  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{CN}^-$ ,  $\text{C}_2\text{O}_4^{2-}$ . They should have an atom containing at least one lone pair of electrons and are attached to the central metal atom or ion with coordinate or covalent bond. The atom in the ligand which donates lone pair of electrons to the central metal atom or ion is called donor atom or coordinating atom. For example, in  $\text{NH}_3$  molecule, nitrogen is the donor atom whereas in  $\text{OH}^-$  ion, oxygen is the donor atom.

The donor atom in the ligand is called as donor site. The ligands may contain one or more donor sites. Depending upon the number of donor sites, the ligands may be classified as :

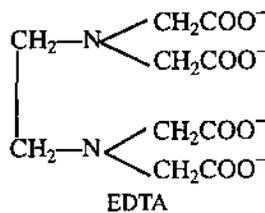
(i) **Monodentate or unidentate ligands :** These ligands can donate only one pair of electrons to the central metal atom or ion. For example,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CO}$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{OH}^-$ ,  $\text{CN}^-$ ,  $\text{NO}_2^-$  are all monodentate ligands.

(ii) **Bidentate ligands :** These ligands have two donor atoms and donate two pairs of electrons to the central metal atom or ion. For example,



Ethylene diamine (en)

(iii) **Polydentate ligands :** The ligands which contain more than two donor atoms in the molecule are called polydentate ligands. These are called tridentate (three donor sites), tetradentate (four donor sites) or hexadentates (six donor sites) depending upon the number of donor atoms present in the molecule. For example, ethylene diamine tetra acetate (EDTA) is a well known hexadentate ligand.



### [IV] Coordination Number

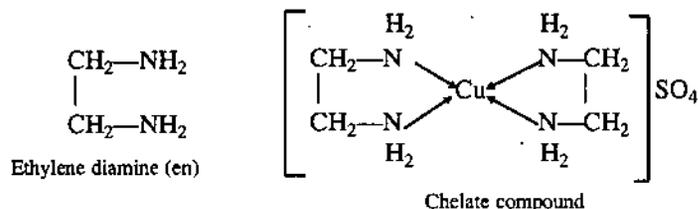
The ligands are attached to the central metal atom or ion through covalent and coordinate bonds. The number of covalent and coordinate bonds formed by the ligands with the central metal atom or ion is known as coordination number of that atom or ion. For example, the coordination numbers of some central metal ions in the complex compounds are given below :

Complex compound	Central metal ion	Ligand	Coordination number
$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$	$\text{Ag}^+$	$\text{NH}_3$	2
$\text{K}_2[\text{Ni}(\text{CN})_4]$	$\text{Ni}^{2+}$	$\text{CN}^-$	4

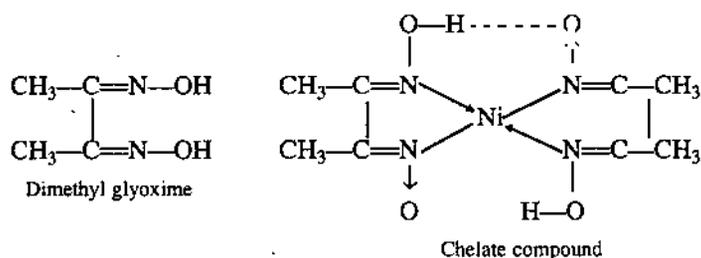
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_3$	$\text{Co}^{3+}$	$\text{NH}_3$ and $\text{Cl}^-$	6
$[\text{Pt}(\text{NH}_3)_4(\text{NO}_2)(\text{Cl})]\text{SO}_4$	$\text{Pt}^{4+}$	$\text{NH}_3, \text{NO}_2^-$ and $\text{Cl}^-$	6
$[\text{Cr}(\text{en})_2(\text{NH}_3)(\text{Br})]\text{Cl}_2$	$\text{Cr}^{3+}$	en, $\text{NH}_3$ , $\text{Br}^-$	6
en = ethylene diamine			(as en is a bidentate ligand and forms two coordinate bonds with central metal ion)

### [V] Chelate Compounds

The cyclic complex compounds formed when a multidentate ligand (ligand having more than one donor site) attached through two or more donor atoms to the same central metal ion are called chelate compounds. In these compounds, the donor atoms are attached to each other as well as to the metal so that metal becomes a part of heterocyclic ring. For example, in the chelate compound  $[\text{Cu}(\text{en})_2]\text{SO}_4$ , the bidentate ligand en (ethylene diamine) is attached to  $\text{Cu}^{2+}$  resulting in the formation of a cyclic structure.

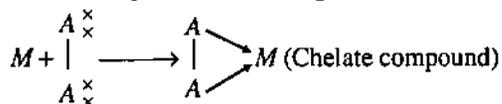


Similarly,  $\text{Ni}^{2+}$  ions form red metal chelate with dimethyl glyoxime. In this chelate, the bidentate ligand dimethyl glyoxime is attached through both the nitrogen atoms to  $\text{Ni}^{2+}$  ions resulting in the formation of a cyclic structure.

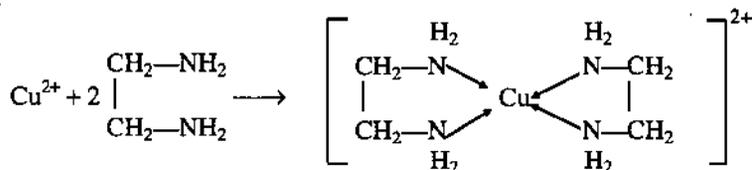


### [VI] Distinction Between Chelate Compound and Complex Compound

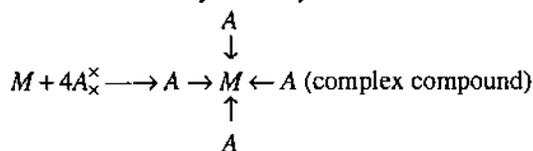
In chelate compound, the metal combines with organic or inorganic molecules or ions which may use two or more donor atoms resulting in the formation of cyclic rings. Thus, the donor groups are firmly attached to the metal ions present in the ring and so chelate compounds are very stable.



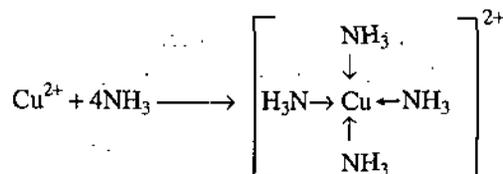
where  $\begin{array}{c} A^{\times} \\ | \\ A^{\times} \end{array}$  is a chelating ligand.



On the other hand, in a complex compound the metal combines with organic or inorganic molecules or ions which may use only one donor-atom so that cyclic rings are not formed.



where  $A^{\times}$  is a monodentate ligand.



The complex compounds are not very stable.

## • 7.2. WERNER'S COORDINATION THEORY

### Werner's Theory of Coordination Compounds :

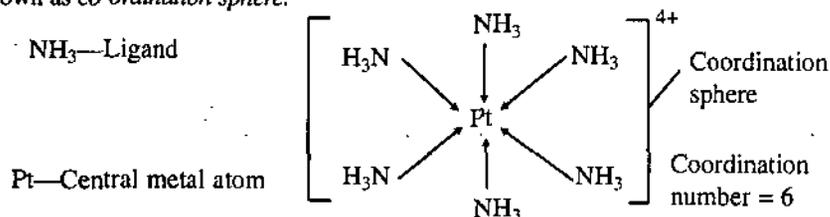
Werner in 1893 gave a theory to explain the structure of co-ordination compounds. The fundamental postulates of this theory are :

(1) Metals possess two types of valency :

(a) **Primary valency or ionizable valency.** This corresponds to the valency or oxidation state of the metal in its simple salts.

(b) **Secondary valency or non-ionic or auxiliary valency.** This corresponds to the coordination number of the metal in the complex salts.

(2) There is a central metal atom around which neutral molecules or anions are coordinated. The neutral molecules or anions are called *ligands* and the number of co-ordinate bonds formed by these ligands is known as *coordination number*. The sphere enclosing the central metal atom and ligands is known as *co-ordination sphere*.



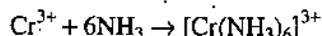
Structure of  $[\text{Pt}(\text{NH}_3)_6]^{4+}$  complex ion.

(3) Each element has a tendency to satisfy both its primary and secondary valencies. The primary valencies are satisfied by negative ions, whereas secondary valencies are satisfied either by negative ions or by neutral molecules. In certain cases, the negative ions may satisfy both the primary and secondary valencies. The primary and secondary valencies of some metal ions are as follows :

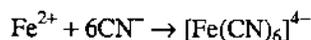
Metal ion	Primary valency	Secondary valency
Cu <sup>2+</sup>	2	4
Ni <sup>2+</sup>	2	4
Pt <sup>2+</sup>	2	4
Cr <sup>3+</sup>	3	6
Co <sup>3+</sup>	3	6
Fe <sup>3+</sup>	3	6

(4) The ligands can be arranged in different ways in space and hence, these compounds are capable of showing the phenomenon of isomerism.

(5) The total charge on the complex ion is the resultant of the charges of central metal atom and ligands.



$$\text{Total charge on complex ion} = +3 + 6 \times 0 = +3$$



$$+2 + 6 \times (-1) = -4$$

**Experimental verification :** Werner applied his theory to give the structures of complexes of platinum with ammonia which are as follows :

### (1) Platinum (IV) Ammine Complex Compounds

#### (a) $\text{PtCl}_4 \cdot 6\text{NH}_3$ :

(i) On treatment with  $\text{AgNO}_3$ , all the four chlorine atoms are precipitated as  $\text{AgCl}$ . This indicates that all the four chlorine atoms are attached to the metal with an ionic bond and are present outside the coordination sphere.

(ii) On treatment with conc.  $\text{H}_2\text{SO}_4$ , all the four chlorine atoms are lost as  $\text{HCl}$  and no  $(\text{NH}_4)_2\text{SO}_4$  is obtained. This indicates that all the six ammonia molecules are attached to the metal with strong bond and are present in the coordination sphere.

(iii) The conductivity measurement shows the presence of five ions.

On the basis of above facts the structure of the complex is as shown in adjacent figure :

**(b)  $\text{PtCl}_4 \cdot 5\text{NH}_3$  :**

(i) On treatment with  $\text{AgNO}_3$ , only three chlorine atoms are precipitated as  $\text{AgCl}$ . This indicates that the three chlorine atoms are attached to the metal with an ionic bond and are present outside the coordination sphere.

(ii) On treatment with conc.  $\text{H}_2\text{SO}_4$ , only three chlorine atoms are lost as  $\text{HCl}$  and no  $(\text{NH}_4)_2\text{SO}_4$  is obtained. This indicates that all the five ammonia molecules and remaining one chlorine atom are attached to the metal with strong bond and are present in the coordination sphere.

(iii) The conductivity measurement shows the presence of four ions.

On the basis of above facts, the structure of the complex is as shown in adjacent figure :

**(c)  $\text{PtCl}_4 \cdot 4\text{NH}_3$  :**

(i) On treatment with  $\text{AgNO}_3$ , only two chlorine atoms are precipitated as  $\text{AgCl}$ . This indicates that the two chlorine atoms are attached to the metal with an ionic bond and are present outside the coordination sphere.

(ii) On treatment with conc.  $\text{H}_2\text{SO}_4$ , only two chlorine atoms are lost as  $\text{HCl}$  and no  $(\text{NH}_4)_2\text{SO}_4$  is obtained. This indicates that all the four ammonia molecules and remaining two chlorine atoms are attached to the metal with strong bond and are present in the coordination sphere.

(iii) The conductivity measurement shows the presence of three ions.

On the basis of above facts, the structure of the complex is as shown.

**(d)  $\text{PtCl}_4 \cdot 3\text{NH}_3$  :**

(i) On treatment with  $\text{AgNO}_3$ , only one chlorine atom is precipitated as  $\text{AgCl}$ . This indicates that only one chlorine atom is attached to the metal with an ionic bond and is present outside the coordination sphere.

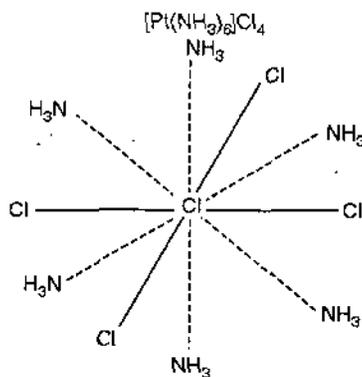
(ii) On treatment with conc.  $\text{H}_2\text{SO}_4$  only one chlorine atom is lost as  $\text{HCl}$  and no  $(\text{NH}_4)_2\text{SO}_4$  is obtained. This indicates that all the three ammonia molecules and remaining three chlorine atoms are attached to the metal with strong bond and are present in the coordination sphere.

(iii) The conductivity measurement shows the presence of two ions.

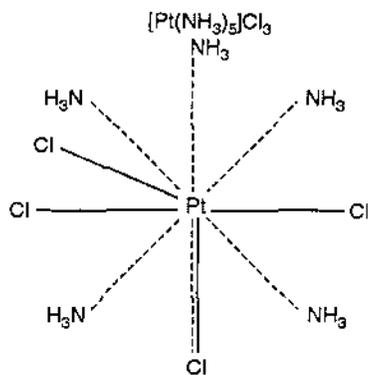
On the basis of above facts, the structure of the complex is as shown.

**(e)  $\text{PtCl}_4 \cdot 2\text{NH}_3$  :**

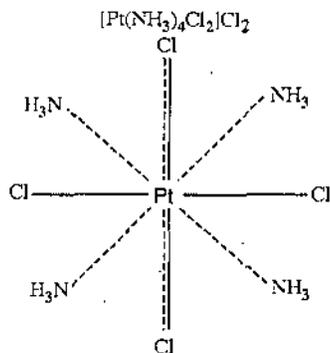
(i) On treatment with  $\text{AgNO}_3$ , no chlorine atom is precipitated as  $\text{AgCl}$ . This indicates that no chlorine atom is attached to the metal with an ionic bond and no chlorine atom is present outside the coordination sphere.



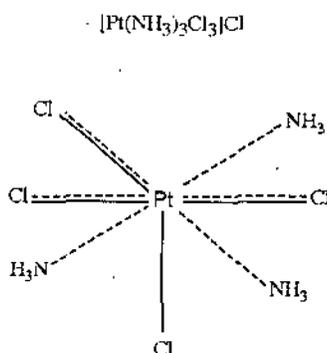
Structure of  $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$



Structure of  $[\text{Pt}(\text{NH}_3)_5]\text{Cl}_3$



Structure of  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$



Structure of  $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$

(ii) On treatment with conc.  $\text{H}_2\text{SO}_4$ , no chlorine atom is lost as  $\text{HCl}$  and no  $(\text{NH}_4)_2\text{SO}_4$  is obtained. This indicates that two ammonia molecules and all the four chlorine atoms are attached to the metal with strong bond and are present in the coordination sphere.

(iii) The conductivity measurement shows the absence of ions.

On the basis of above facts, the structure of the complex is as shown.

## (2) Platinum (II) Ammine Complex Compounds :

### (a) $\text{PtCl}_2 \cdot 4\text{NH}_3$ :

(i) On treatment with  $\text{AgNO}_3$ , both the chlorine atoms are precipitated as  $\text{AgCl}$ . This indicates that both the chlorine atoms are attached to the metal with an ionic bond and are present outside the coordination sphere.

(ii) On treatment with conc.  $\text{H}_2\text{SO}_4$ , both the chlorine atoms are lost as  $\text{HCl}$  and no  $(\text{NH}_4)_2\text{SO}_4$  is obtained. This indicates that all the four ammonia molecules are attached to the metal with strong bond and are present in the coordination sphere.

(iii) The conductivity measurement shows the presence of three ions.

On the basis of above facts the structure of the complex is as shown.

### (b) $\text{PtCl}_2 \cdot 3\text{NH}_3$ :

(i) On treatment with  $\text{AgNO}_3$ , only one chlorine atom is precipitated as  $\text{AgCl}$ . This indicates that only one chlorine atom is attached to the metal with an ionic bond and is present outside the coordination sphere.

(ii) On treatment with conc.  $\text{H}_2\text{SO}_4$ , only one chlorine atom is lost as  $\text{HCl}$  and no  $(\text{NH}_4)_2\text{SO}_4$  is obtained. This indicates that three ammonia molecules and remaining one chlorine atom are attached to the metal with strong bond and are present in the coordination sphere.

(iii) The conductivity measurement shows the presence of two ions.

On the basis of above facts, the structure of the complex is as shown.

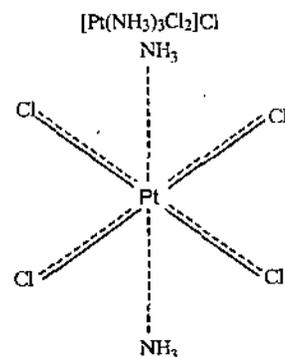
### (c) $\text{PtCl}_2 \cdot 2\text{NH}_3$ :

(i) On treatment with  $\text{AgNO}_3$ , no chlorine atom is precipitated as  $\text{AgCl}$ . This indicates that no chlorine atom is attached to the metal with an ionic bond and no chlorine atom is present outside the coordination sphere.

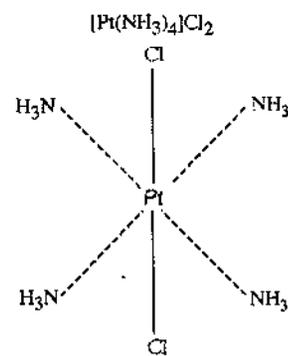
(ii) On treatment with conc.  $\text{H}_2\text{SO}_4$ , no chlorine atom is lost as  $\text{HCl}$  and no  $(\text{NH}_4)_2\text{SO}_4$  is obtained. This indicates that two ammonia and two chlorine atoms are attached to the metal with strong bond and are present in the coordination sphere.

(iii) The conductivity measurement shows the absence of ions.

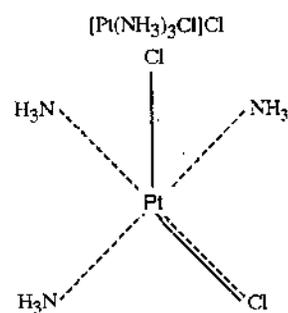
On the basis of above facts, the structure of complex is as shown.



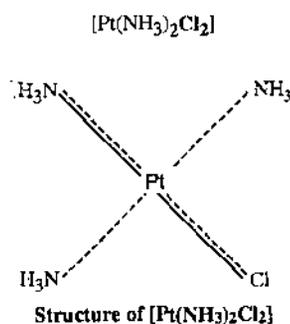
Structure of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$



Structure of  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$



Structure of  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}$

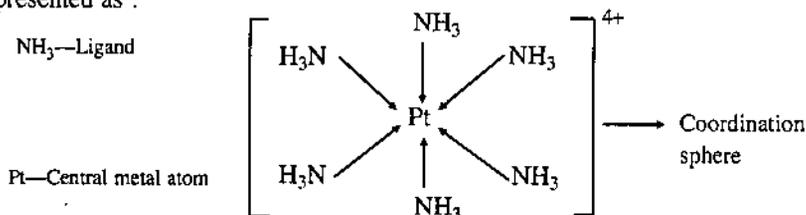


Structure of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

## • 7.3. SIDWICK INTERPRETATION OF CO-ORDINATION COMPOUNDS

**Electronic Interpretation.** Sidwick and Lowry gave the electronic interpretation of Werner's theory of coordination compounds. According to them primary valencies result from the transference of electrons, whereas secondary valencies result from the sharing of electrons, i.e. there is a formation of electrovalent bond in primary valencies and coordinate bond in secondary valencies. They also pointed out that all ligands (neutral molecules or anions) have atoms with at least one lone pair of electrons. They donate this lone pair of electrons to the central metal ion and

form coordinate bond. The number of coordinate bonds formed between the ligands and the central metal ion represent the secondary valency or coordination number of the central metal ion. The atom which donates the pair of electrons is known as donor and the central metal atom which receives it is known as acceptor and the coordinate bond is represented by an arrow head ( $\rightarrow$ ) pointing away from donor towards acceptor atom. For example, the structure of  $[\text{Pt}(\text{NH}_3)_6]^{4+}$  ion may be represented as :



The stability of complex compounds was explained on the basis of effective atomic number. According to them, in most of the complex ions the effective atomic number of central metal atom becomes equal to the atomic number of next inert gas. The effective atomic number of metal in the complex compound is the sum of electrons present in the metal ion and the total number of electrons donated by the ligands. It is represented by the formula :

Effective atomic number = Atomic number of metal – oxidation state of the metal in the complex compound + total number of electrons donated by the ligands.

For example, in the complex  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , the atomic number of cobalt is 27 and oxidation state of cobalt is +3. Six ammonia molecules are attached to the cobalt and each molecule gives two electrons. Thus, the effective atomic number of cobalt =  $27 - 3 + 6 \times 2 = 36$  which is equal to the atomic number of krypton. The effective atomic numbers of some metals in the complex compounds are given in the following table.

Complex ion	Central metal atom	Atom no.	Oxidation state of metal in the complex ion	Number of electrons donated by ligands	Effective atomic number
$[\text{Fe}(\text{CN})_6]^{4-}$	Fe	26	+2	$6 \times 2 = 12$	$26 - 2 + 12 = 36$
$[\text{Cu}(\text{CN})_4]^{3-}$	Cu	29	+1	$4 \times 2 = 8$	$29 - 1 + 8 = 36$
$[\text{Co}(\text{NO}_2)_6]^{3-}$	Co	27	+3	$6 \times 2 = 12$	$27 - 3 + 12 = 36$
$[\text{Ni}(\text{CO})_4]$	Ni	28	0	$4 \times 2 = 8$	$28 - 0 + 8 = 36$
$[\text{Pt}(\text{NH}_3)_6]^{4+}$	Pt	78	+4	$6 \times 2 = 12$	$78 - 4 + 12 = 86$
$[\text{Fe}(\text{CN})_6]^{3-}$	Fe	26	+3	$6 \times 2 = 12$	$26 - 3 + 12 = 35$
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	Cr	24	+3	$6 \times 2 = 12$	$24 - 3 + 12 = 33$
$[\text{Pt}(\text{NH}_3)_4]^{2+}$	Pt	78	+2	$4 \times 2 = 8$	$78 - 2 + 8 = 84$
$[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$	Cr	24	+3	$4 \times 2 + 2 \times 2 = 12$	$24 - 3 + 12 = 33$
$[\text{Co}(\text{en})_2\text{Cl}_2]^+$	Co	27	+3	$2 \times 4 + 2 \times 2 = 12$ by en by Cl	$27 - 3 + 12 = 36$

From the above table, it is clear that in most of the cases, the effective atomic number of central metal atom is equal to the atomic number of next inert gas but it has some exceptions also. Hence, the tendency to attain an inert gas configuration is not a necessary condition for the stability of complex compounds.

**Objections :** Sidwick's electronic interpretation of coordination compounds is not entirely satisfactory. Some objections are :

(1) There will be an accumulation of negative charge on the central metal ion by the donation of electron pairs from ligands, thus, central metal ion will become negatively charged with respect to ligands.

(2) The electron pair available for donation in ammonia, water and many other neutral molecules is s-electron pair which has no bonding characteristics on the basis of available energy.

#### • 7.4. IUPAC NOMENCLATURE OF CO-ORDINATION COMPOUNDS

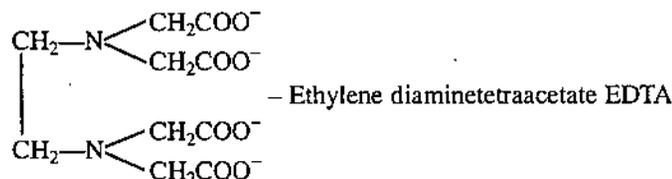
The following rules are observed in naming the complex compounds :

**(1) Order of naming ions :** In ionic complex, positive ion is named first followed by negative ion. For example, in naming complex compound,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , the name of positive ion  $[\text{Co}(\text{NH}_3)_6]^{3+}$  [Hexamine cobalt (III)] is written first and name of negative ion  $\text{Cl}^-$  (chloride) is written afterwards. Similarly in naming complex compound,  $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$ , the name of positive ion  $\text{K}^+$  (potassium) is written first and name of negative ion  $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$  [trioxalato aluminate (III)] is written afterwards. In the non-ionic or molecular complex one word name is given. For example, name of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  is written as diamminedichloroplatinum (II).

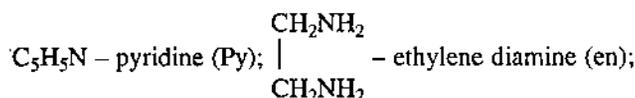
**(2) Naming of coordination sphere :** In naming complex ions, the ligands (coordinating groups) are named first. If the ligands have simple names, their number is indicated by the prefixes di, tri, tetra etc. If the ligands have complicated names (e.g., ethylene diamine (en), pyridine (py) etc.), their number is indicated by the prefixes bis, tris, tetrakis etc. and names of such ligands are written in the bracket.

**(3) Naming of ligands :** In complex compounds, central metal ion is attached with negative, neutral or positive ligands.

(a) If the ligand is anion (negatively charged), it is named as ending in 'O'. For example :  $\text{CO}_3^{2-}$  – carbonato;  $\text{SO}_3^{2-}$  – sulphito;  $\text{CH}_3\text{COO}^-$  – acetato;  $\text{NO}_2^-$  – nitro;  $\text{ONO}^-$  – nitrito;  $\text{NO}_3^-$  – nitrato;  $\text{Cl}^-$  – chloro;  $\text{Br}^-$  – bromo;  $\text{I}^-$  – iodo;  $\text{OH}^-$  – hydroxo;  $\text{O}^{2-}$  – oxo;  $\text{O}_2^{2-}$  – peroxy;  $\text{O}_2^-$  – superoxy;  $\text{CN}^-$  – cyano;  $\text{SO}_4^{2-}$  – sulphato;  $\text{S}_2\text{O}_3^{2-}$  – thiosulphato;  $\text{SCN}^-$  – thio cyanato;  $\text{NCS}^-$  – isothiocyanato;  $\text{NH}_2^-$  – amido;  $\text{NH}^-$  – imido;  $\text{N}_3^-$  – azido;  $\text{C}_2\text{O}_4^{2-}$  – oxalato,



(b) If ligand is neutral, it is named as such



$(\text{C}_6\text{H}_5)_3\text{P}$  – Tri phenyl phosphine ( $\text{PPh}_3$ ).

The following examples are, however, exceptions :

$\text{H}_2\text{O}$  – aquo;  $\text{NH}_3$  – ammine;  $\text{NO}$  – nitrosyl;  $\text{CO}$  – carbonyl.

(c) Positive ligands which are rare, end in -ium. For example:  $\text{NH}_2\text{–NH}_3^+$  – hydrazinium;  $\text{NO}^+$  – nitrosylium,  $\text{NO}_2^+$  – Nitronium.

**(4) Order of naming ligands :** If two or more types of ligands are present, according to modern IUPAC system, they are written in the alphabetical order irrespective of whether they are negative or neutral. For example, in the complex compound  $[\text{Pt}(\text{NH}_3)_4(\text{Cl})(\text{NO}_2)]\text{Cl}_2$ , the order of naming ligands is ammine chloro nitro.

**(5) Naming of bridging groups :** In the polynuclear complexes (the complexes having two or more metal atoms), the bridging group is indicated by separating it from rest of the complex by hyphens and by adding  $\mu$ - before its name. The Greek letter  $\mu$  is indicated before the name of each bridging group.

**(6) Name and oxidation state of central metal ion :** After indicating the number and names of ligands, the next step is to mention the name of central metal ion followed by a Roman numeral such as II, III, IV to indicate the oxidation state of the metal. If the complex ion is a cation, the central metal ion is named by its usual name. Thus,  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  is named as hexammine chromium (III) ion. If the complex ion is anion, the name of central metal ion is made to end in 'ate'. Thus,  $[\text{Ni}(\text{CN})_4]^{2-}$  is named as tetra cyano nickelate (II) ion.

The following examples will make the above rules clear.

**(1) Ionic complexes in which metal forms a part of complex cation (cationic complexes) :**

(a)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  – Hexammine cobalt (III) chloride.

(b)  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  – Diammine silver (I) chloride.

(c)  $[\text{Cr}(\text{en})_3]\text{Cl}_3$  – Tris (ethylene diamine) chromium (III) chloride.

(d)  $[\text{Pt}(\text{py})_4]\text{Cl}_2$  – Tetrakis (pyridine) platinum (II) chloride.

(e)  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  – Tetrammine copper (II) sulphate.

**(2) Ionic complexes in which metal forms a part of complex anion (anionic complexes) :**

(a)  $\text{K}_4[\text{Fe}(\text{CN})_6]$  – Potassium hexacyanoferrate (II).

(b)  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$  – Sodium hexanitrocobaltate (III).

(c)  $\text{K}_3[\text{Cu}(\text{CN})_4]$  – Potassium tetracyanocuprate (I).

(d)  $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$  – Potassium trioxalatoaluminate (III).

(e)  $\text{Na}_2[\text{SiF}_6]$  – Sodium hexafluorosilicate (IV).

(f)  $\text{K}[\text{Ag}(\text{CN})_2]$  – Potassium dicyanoargentate (I).

**(3) Ionic complexes in which metal forms a part of complex cation as well as complex anion :**

(a)  $[\text{Co}^{\text{III}}(\text{NH}_3)_6] [\text{Cr}^{\text{III}}(\text{C}_2\text{O}_4)_3]$  – Hexammine cobalt (III) trioxalato chromate (III).

(b)  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$  – Tetrammine platinum (II) tetra chloro platinate (II).

(c)  $[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{CN})_6]$  – Hexammine chromium (III) hexacyano cobaltate (III).

(d)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]$  – Tetrammine dichloro platinum (IV) tetra chloro platinate (II).

**(4) Molecular or non-ionic complexes :**

(a)  $[\text{Ni}(\text{CO})_4]$  – Tetra carbonyl nickel (0).

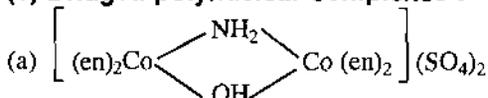
(b)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  – Diammine dichloro platinum (II).

(c)  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$  – Triammine trinitro cobalt (III).

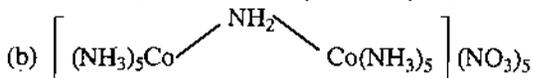
(d)  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)(\text{Cl})(\text{CN})]$  – Triammine chloro cyano nitro cobalt (III).

(e)  $[\text{Pt}(\text{py})(\text{NH}_3)(\text{NO}_2)(\text{Cl})(\text{Br})(\text{I})]$  – Ammine bromo chloro iodo nitro (pyridine) platinum.

**(5) Bridged polynuclear complexes :**



Tetrakis (ethylene diamine)  $\mu$ -amido  $\mu$ -hydroxo dicobalt (III) sulphate.



Decammine  $\mu$ -amido di cobalt (III) nitrate.

**(6) Complex cations :**

(a)  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  – Tetrammine platinum (II) ion.

(b)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  – Hexaquo chromium (III) ion.

(c)  $[\text{Cr}(\text{en})_2(\text{NH}_3)(\text{Br})]^{2+}$  – Ammine bromo bis (ethylene diamine) chromium (III) ion.

(d)  $[\text{Pt}(\text{NH}_3)_4(\text{NO}_2)(\text{Cl})]^{2+}$  – Tetrammine chloro nitro platinum (IV) ion.

**(7) Complex anions :**

(a)  $[\text{Cr}(\text{CN})_6]^{3-}$  – Hexacyano chromate (III) ion.

(b)  $[\text{CoCl}_6]^{3-}$  – Hexachloro cobaltate (III) ion.

(c)  $[\text{Fe}(\text{CN})_6]^{3-}$  – Hexacyano ferrate (III) ion.

(d)  $[\text{Zn}(\text{OH})_4]^{2-}$  – Tetrahydroxo zincate (II) ion.

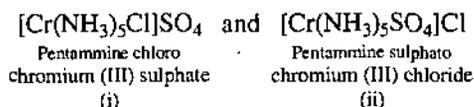
(e)  $[\text{Pb}(\text{OH})_4]^{2-}$  – Tetrahydroxo plumbate (II) ion.

## • 7.5. ISOMERISM IN CO-ORDINATION COMPOUNDS

Compounds having the same molecular formula but having different physical or chemical properties are called isomers and the phenomenon is known as isomerism. In coordination compounds, this isomerism is due to the difference in the structure of the compounds or due to the difference in the relative arrangement of atoms or groups in space. On this basis, isomerism among the coordination compounds is mainly of two types :

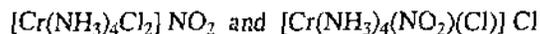
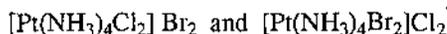
**(1) Structural isomerism.** When two or more compounds have the same molecular formula but have different structures, they are said to exhibit structural isomerism. This isomerism is of following types —

**(a) Ionization isomerism.** The complex compounds which have the same molecular formula but which give different ions in solution are called ionization isomers and the phenomenon is known as ionization isomerism. In these compounds there is a difference in the position of groups inside and outside the coordination sphere. For example,

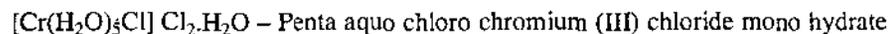
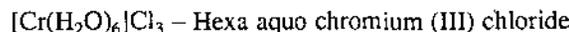


The compound (i) gives white precipitate with  $\text{BaCl}_2$  solution but gives no precipitate with  $\text{AgNO}_3$  solution, whereas compound (ii) gives white precipitate with  $\text{AgNO}_3$  solution but gives no precipitate with  $\text{BaCl}_2$  solution.

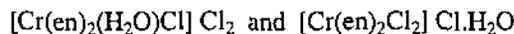
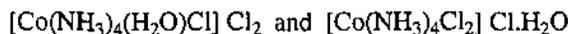
Some other complexes showing this type of isomerism are :



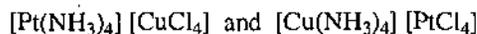
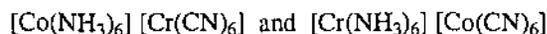
**(b) Hydration isomerism.** This type of isomerism arises due to the difference in the position of water molecules in the complex, which may be present inside or outside the coordination sphere. When the water molecules are present outside the coordination sphere, they can be easily removed but when they are present inside they cannot be removed even on heating. This is because in such cases, there is a formation of strong bond between metal and water molecules. For example, the molecular formula,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  exists in the following three isomers —



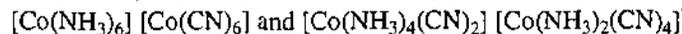
Some other complexes showing this isomerism are —



**(c) Co-ordination isomerism.** This type of isomerism is found in those complex compounds in which both positive and negative ions are complex ions. The isomerism arises due to the exchange of ligands between two complex ions. For example,



This type of isomerism is also found in those complex compounds in which same metal atom is present in both the complex ions.



**(d) Linkage isomerism.** This type of isomerism is found in those complex compounds where a ligand contains more than one donor atom. The unidentate ligands which can bind to the central metal atom through two donor atoms are called ambidentate ligands. For example —

(i) In  $\text{NO}_2$  group both nitrogen and oxygen may act as donor atom.

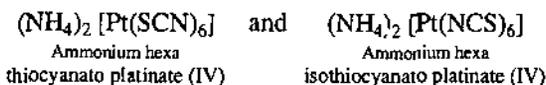
(ii) In  $\text{SCN}$  (sulpho cyanide) group both nitrogen and sulphur may act as donor atoms.

Thus, donation of electron pairs by different atoms will form different compounds. For example,

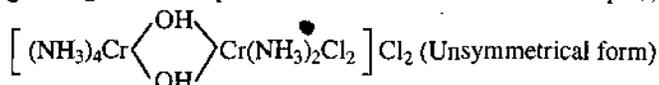
$[\text{Cr}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$  - Pentammine nitro chromium (III) chloride - In this compound, nitrogen atom donates lone pair of electrons to the metal atom.

$[\text{Cr}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$  - Pentammine nitrito chromium (III) chloride - In this compound, oxygen atom donates lone pair of electrons to the metal atom.

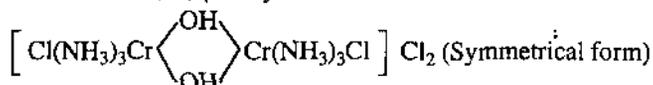
Some other complexes showing this isomerism are —



**(e) Co-ordination position isomerism.** This type of isomerism is found in bridged polynuclear complexes and arises due to exchange of ligands between two metal atoms. In this isomerism exchange of ligands takes place within the same ion. For example,

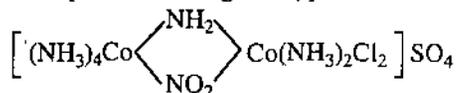


Tetrammine chromium (III)  $\mu$ -dihydroxo diammine dichloro chromium (III) chloride.

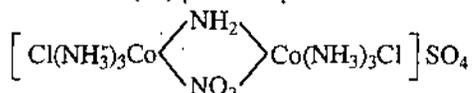


Triammine chloro chromium (III)  $\mu$ -dihydroxo triammine chloro chromium (III) chloride.

Some other complexes showing this type of isomerism are —



Tetrammine cobalt (III)  $\mu$ -amido  $\mu$ -nitro diammine dichloro cobalt (III) sulphate and

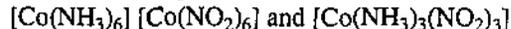


Triammine chloro cobalt (III)  $\mu$ -amido  $\mu$ -nitro triammine chloro cobalt (III) sulphate.

From the above examples, it is clear that arrangement of  $\text{NH}_3$  and  $\text{Cl}$  ligands is different relative to two chromium or two cobalt atoms.

**(f) Polymerization isomerism.** This type of isomerism is found in those complex compounds where the two isomers have the same empirical formula but different molecular weights. These complex compounds have the same ratio of metal atoms and ligands in them. For example,  $[\text{Pt}(\text{NH}_3)_4] [\text{PtCl}_4]$  and  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ .

The ratio of  $\text{Pt} : \text{NH}_3 : \text{Cl}$  is 1 : 2 : 2 in both the complexes. The other examples are :



Polymerization isomerism is not isomerism in the real sense.

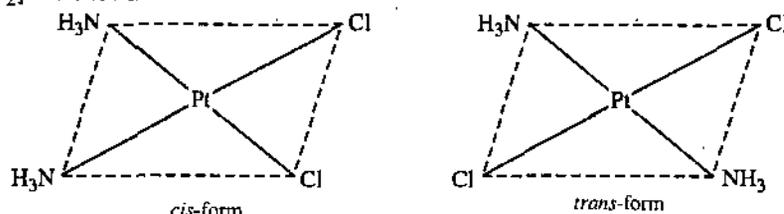
**(2) Stereo isomerism.** When two or more compounds have the same molecular formula but have different arrangement of atoms or groups in space they are said to exhibit stereo isomerism. This isomerism is of following types :

**(a) Geometrical isomerism.** This isomerism arises due to different geometrical arrangements of ligands around the central metal atom. In the *cis* form two similar ligands occupy adjacent positions in space, whereas in the *trans* form two similar ligands occupy opposite positions in space. This type of isomerism is also known as *cis-trans isomerism*.

This type of isomerism is found in those complex compounds in which central metal ion has a co-ordination number 4 or 6.

**(i) Co-ordination number 4** — The co-ordination number 4 is found in tetrahedral or square planar complexes. The *cis-trans* isomerism is not found in tetrahedral complexes because all the four ligands are at equal distance from the central metal atom. However, this type of isomerism is very common in square planar complexes. In general, the square planar complexes having the general formula  $[\text{MA}_2\text{B}_2]^{n\pm}$ ,  $[\text{MA}_2\text{BC}]^{n\pm}$ ,  $[\text{MABCD}]^{n\pm}$  and  $[\text{M}(\text{AB})_2]^{n\pm}$  show geometrical isomerism where  $A$ ,  $B$ ,  $C$  and  $D$  are monodentate ligands and  $\text{AB}$  is unsymmetrical bidentate ligand. On the other hand, the complexes having the general formula  $[\text{MA}_4]^{n\pm}$ ,  $[\text{MA}_3\text{B}]^{n\pm}$  or  $[\text{MAB}_3]^{n\pm}$  do not show this type of isomerism.

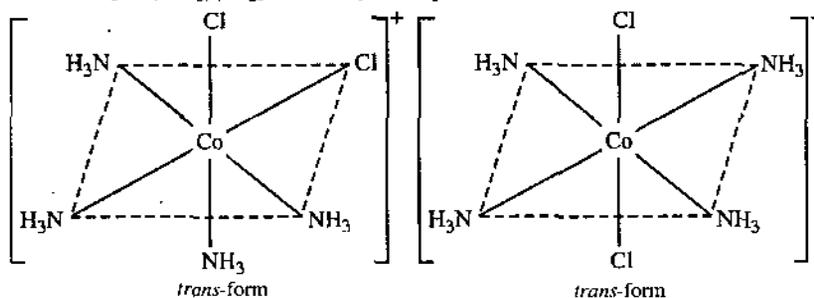
**Complexes of the type  $[\text{MA}_2\text{B}_2]^{n\pm}$**  — The most common examples of the complexes of this type are  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ ,  $[\text{Pt}(\text{py})_2\text{Cl}_2]$  and  $[\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2]$ . The *cis-trans* isomers of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  are shown below :



*cis* and *trans* isomers of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

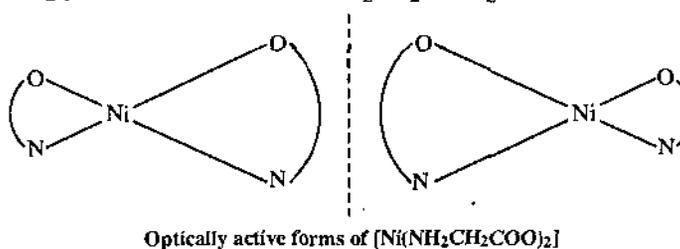
(ii) **Coordination number 6** — The coordination number 6 is found in octahedral complexes. The complexes having the general formula,  $[MA_4B_2]^{n\pm}$ ,  $[MA_4BC]^{n\pm}$ ,  $[MA_3B_3]^{n\pm}$ ,  $[MABCDXY]^{n\pm}$ ,  $[M(AA)_2B_2]^{n\pm}$ ,  $[M(AA)_2BC]^{n\pm}$  and  $[M(AB)_3]^{n\pm}$  show the phenomenon of geometrical isomerism, where A, B, C, D, X, Y are monodentate ligands, AA and AB are symmetrical and unsymmetrical bidentate ligands, respectively. The octahedral complexes of the type  $[MA_6]^{n\pm}$ ,  $[MA_5B]^{n\pm}$  and  $[MAB_5]^{n\pm}$  do not show geometrical isomerism. This is because in these complexes different arrangements of the ligands in space are not possible.

**Complexes of the type  $[MA_4B_2]^{n\pm}$  or  $[MA_4BC]^{n\pm}$**  — The most common examples of the complexes of this type are  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ ,  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$  and  $[\text{Cr}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]^+$  ions. The cis-trans isomers of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  ion may be represented as —



(b) **Optical isomerism** — The compounds having identical physical and chemical properties but differing in their behaviour towards polarized light are called optical isomers and the phenomenon is known as optical isomerism. The isomer which rotates the plane of polarized light in clockwise direction is known as *dextro rotatory* or *d-form* and the isomer which rotates the plane of polarized light in anti clockwise direction is known as *laevo rotatory* or *l-form*. The *d-* and *l-* forms of a compound are always related to each other as object to image and are called *enantiomorphs*. For a compound to show optical isomerism, it should be asymmetric, i.e., it should not have a plane of symmetry in its structure. This type of isomerism is found in those complex compounds in which central metal ion has a coordination number 4 or 6.

(i) **Coordination number 4** — The coordination number 4 of central metal ion is found in tetrahedral or square planar complexes. The tetrahedral complexes of the type  $[M(AB)_2]^{n\pm}$  containing unsymmetrical bidentate ligands show optical activity. The most common examples of this type are bis (glycinato) nickel (II), bis (benzoyl acetonato) beryllium (II). The two optically active forms of *bis* (glycinato) nickel (II),  $[\text{Ni}(\text{NH}_2\text{CH}_2\text{COO})_2]$  are shown below —

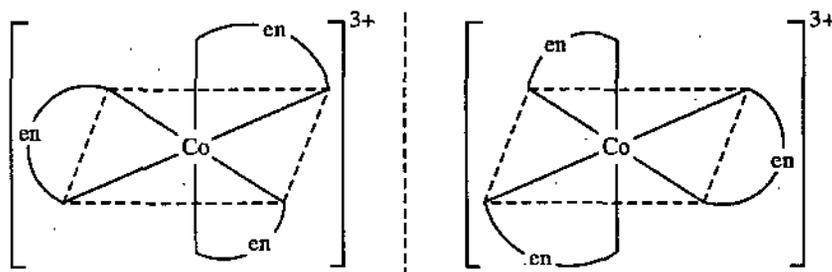


The square planar complexes do not show optical activity. In these complexes all the four ligands and central metal atom lie in the same plane and, therefore, they contain a plane or axis of symmetry.

(ii) **Coordination number 6** — The coordination number 6 is found in octahedral complexes. Such complexes show the phenomenon of optical isomerism. The complexes having the general formula  $[MA_2X_2Y_2]^{n\pm}$ ,  $[MA_2X_2YZ]^{n\pm}$ ,  $[MA_2XYZL]^{n\pm}$  or  $[MABXYZL]^{n\pm}$  show optical isomerism. In these complexes all the ligands are monodentates.

The octahedral complexes of the general formula  $[M(AA)_3]^{n\pm}$ ,  $[M(AA)_2X_2]^{n\pm}$ ,  $[M(AA)_2XY]^{n\pm}$ ,  $[M(AA)X_2Y_2]^{n\pm}$  show optical isomerism where AA is symmetrical bidentate ligand and X and Y are monodentate ligands.

**Complexes of the type  $[M(AA)_3]^{n\pm}$**  — The most common examples of the complexes of this type are  $[\text{Co}(\text{en})_3]^{3+}$  (en = ethylene diamine) and  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ . The optically active isomers of  $[\text{Co}(\text{en})_3]^{3+}$  ion are shown ahead —

Optically active isomers of  $[\text{Co}(\text{en})_3]^{3+}$  ion.

## • 7.6. VALENCY BOND THEORY

Valency bond theory was proposed by Pauling (1931). The theory is concerned with the electronic structure of the central metal ion in the ground state, bonding, geometry and magnetic properties of the complexes. The main postulates of this theory are —

(i) The central metal atom or ion in the complex makes available a number of empty orbitals for the formation of co-ordinate bonds with suitable ligands. The number of empty orbitals available for this purpose is equal to the coordination number of the central metal atom or ion.

(ii) The empty orbitals ( $s$ ,  $p$  or  $d$ ) of the central metal atom or ion hybridize to give an equal number of hybrid orbitals of same energy. These hybrid orbitals have the definite geometry. The following types of hybridization take place in the formation of complexes —

Co-ordination number	Hybridization	Geometry	Examples
2.	$sp$	Linear	$[\text{Ag}(\text{NH}_3)_2]^+$ , $[\text{Ag}(\text{CN})_2]^-$
3.	$sp^2$	Trigonal planar	$[\text{HgI}_3]^-$
4.	$sp^3$	Tetrahedral	$[\text{Ni}(\text{CO})_4]$ , $[\text{Zn}(\text{NH}_3)_4]^{2+}$
5.	$d\ sp^2$	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{Pt}(\text{NH}_3)_4]^{2+}$ , $[\text{Cu}(\text{NH}_3)_4]^{2+}$
6.	$d^2sp^3$	Inner orbital octahedral	$[\text{Fe}(\text{CN})_6]^{4-}$ , $[\text{Cr}(\text{NH}_3)_6]^{3+}$ , $[\text{Co}(\text{NH}_3)_6]^{3+}$
7.	$sp^3d^2$	Outer orbital octahedral	$[\text{FeF}_6]^{3-}$ , $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

(iii) The  $d$ -orbitals of the central metal atom or ion involved in hybridization may be inner *i.e.*  $(n-1)d$  or the outer  $nd$  orbitals. For example, in the formation of octahedral complex, the orbitals involved may be two  $3d$ , one  $4s$  and three  $4p$  ( $d^2sp^3$ ) or one  $4s$ , three  $4p$  and two  $4d$  ( $sp^3d^2$ ).

(iv) Complexes formed by using inner  $d$ -orbitals contain smaller number of unpaired electrons and are known as inner orbital, low spin or spin paired complexes whereas complexes formed by using outer  $d$ -orbitals contain a large number of unpaired electrons and are known as outer orbital, high spin or spin free complexes.

(v) Each ligand has at least one orbital containing a lone pair of electrons.

(vi) When ligands approach the central metal atom or ion, the empty hybrid orbitals of the central metal atom or ion overlap with the filled orbitals of the ligand to form ligand-metal coordinate bond. The number of such bonds depends on the number of empty orbitals made available by the central metal atom or ion.

(vii) The non-bonding electrons of the central metal atom or ion present in the inner orbitals do not take part in the bond formation.

(viii) If the complex contains one or more unpaired electrons, it is paramagnetic and if it contains all the electrons paired, it is diamagnetic.

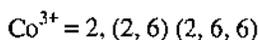
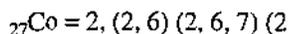
(ix) During complex formation, Hund's rule of maximum multiplicity is strictly followed. The electrons may be forced to pair up against Hund's rule only when the ligands are strong.

### (1) Metal-ligand bond in octahedral complexes

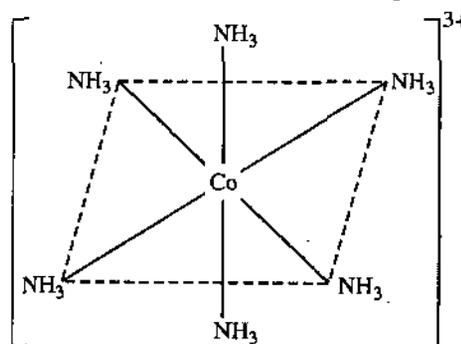
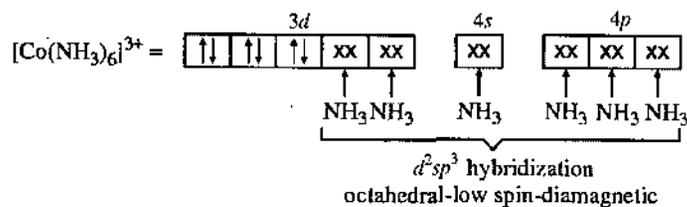
These complexes are formed either by  $d^2sp^3$  or  $sp^3d^2$  hybridization. Since  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals lie directly in the path of ligands, these orbitals are used in the formation of these complexes.

The formation, structures, shapes and magnetic properties of some of the octahedral complexes are discussed here —

(a) **Hexammine cobalt (III) ion,  $[\text{Co}(\text{NH}_3)_6]^{3+}$**  — In this complex ion, cobalt is present as  $\text{Co}^{3+}$  whose electronic configuration is —



When six  $\text{NH}_3$  molecules approach  $\text{Co}^{3+}$  ion to form  $[\text{Co}(\text{NH}_3)_6]^{3+}$  complex ion, the unpaired electrons of the  $\text{Co}^{3+}$  ion are forced to pair up by these strong ligands against Hund's rule and six empty orbitals are available for hybridization. Now  $d^2sp^3$  hybridization takes place in the  $\text{Co}^{3+}$  ion which gives six equivalent  $d^2sp^3$  hybrid orbitals to form  $[\text{Co}(\text{NH}_3)_6]^{3+}$ .

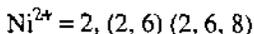
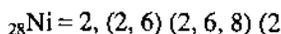


Structure of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  complex ion

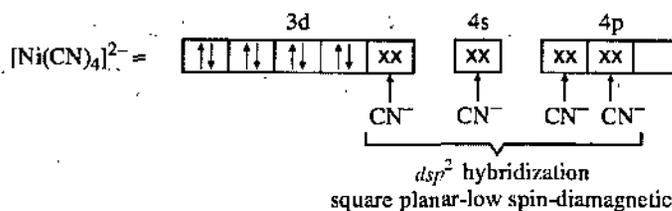
Since inner 3d orbitals are used for bond formation, it is called inner orbital complex. Such complexes are more stable than the outer orbital complexes. Due to less number of unpaired electrons, it is a low spin complex and is diamagnetic as it does not contain an unpaired electron.

**(2) Metal ligand bond in square planar complexes :**

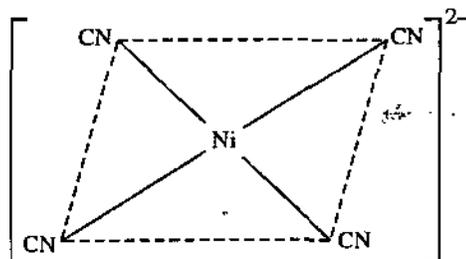
(a) **Tetracyano nickelate (II) ion,  $[\text{Ni}(\text{CN})_4]^{2-}$**  — In this complex ion, Nickel is present as  $\text{Ni}^{2+}$  whose electronic configuration is —



When four  $\text{CN}^-$  ions approach  $\text{Ni}^{2+}$ , pairing of electrons takes place. In this way all the eight electrons in 3d orbitals are paired and one empty d-orbital is available for  $dsp^2$  hybridization and  $[\text{Ni}(\text{CN})_4]^{2-}$  ion is formed as —



Since in this complex ion, all the electrons are paired, hence it is diamagnetic and will have low spin. The complex is square planar due to  $dsp^2$  hybridization.


 Structure of  $[\text{Ni}(\text{CN})_4]^{2-}$  complex ion.

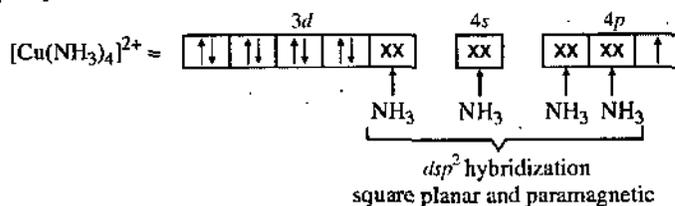
(b) **Tetrammine copper (II) ion,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$**  — In this complex ion, copper is present as  $\text{Cu}^{2+}$  whose electronic configuration is —

$${}_{29}\text{Cu} = 2, (2, 6) (2, 6, 10) (1)$$

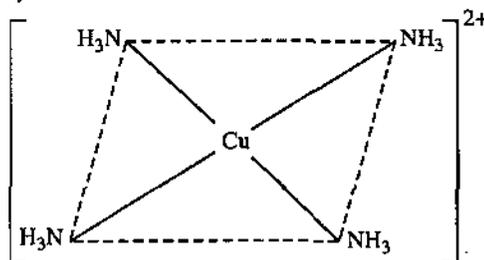
$$\text{Cu}^{2+} = 2, (2, 6) (2, 6, 9)$$



In the presence of strong ligand  $\text{NH}_3$ , copper forms complexes with  $dsp^2$  hybridization. In this case one unpaired electron of 3d orbital is promoted to 4p orbital so that one empty 3d orbital is involved in  $dsp^2$  hybridization as shown below —



The complex ion is weakly paramagnetic due to the presence of one unpaired electron and is square planar due to  $dsp^2$  hybridization.


 Structure of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  complex ion.

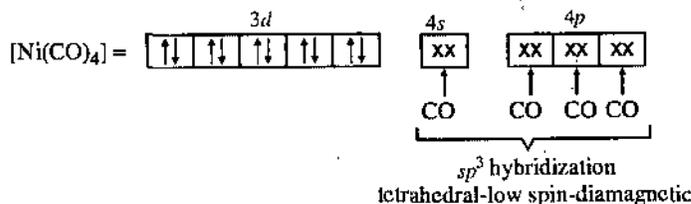
### (3) Metal ligand bond in tetrahedral complexes

**Tetracarbonyl nickel (0),  $[\text{Ni}(\text{CO})_4]$**  — In this complex, the oxidation state of nickel is zero. The electronic configuration of nickel is —

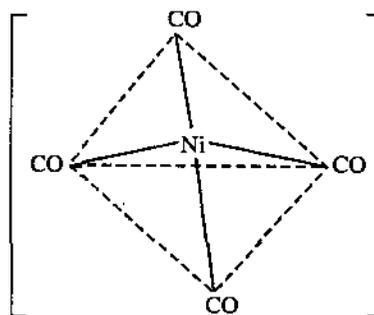
$${}_{28}\text{Ni} = 2, (2, 6) (2, 6, 8) (2)$$



Since CO is a strong ligand, they force the 4s electrons to pair with the 3d orbital electrons. This results in  $sp^3$  hybridization and tetrahedral structure.



Since in this complex, all the electrons are paired, hence it is diamagnetic and will have low spin,

Structure of  $[\text{Ni}(\text{CO})_4]$ 

### Limitations of Valency Bond Theory

- (1) This theory does not explain the formation of five coordinate complexes.
- (2) It does not explain the spectra of complexes.
- (3) This theory considers the orbitals of central metal atom and importance to orbitals of ligands has not been given.
- (4) It does not give any satisfactory explanation of inner and outer orbital complexes.
- (5) It does not give any satisfactory explanation for the geometry of the complexes of same metal in different compounds. In some complexes, the electrons pair up against Hund's rule whereas in others electronic configuration is not disturbed.
- (6) This theory does not explain whether a four coordinate complex will be tetrahedral or square planar.
- (7) This theory does not explain the reaction rate and mechanism of reactions.
- (8) It gives no explanation of the colour observed for complex ion.
- (9) It does not give any idea about splitting of  $d$ -energy levels.
- (10) It does not explain any distortion in symmetrical complex compounds.

### • 7.7. INNER AND OUTER ORBITAL COMPLEXES

The central metal atom or ion may use inner  $(n-1)d$  orbitals or outer  $nd$  orbitals for hybridization. On this basis the complexes may be classified as,

**Inner orbital complexes :** The complexes which use inner  $d$ -orbitals, i.e.,  $(n-1)d$  orbitals of the central metal atom or ion for bond formation are called inner orbital complexes. These complexes are formed by strong ligands i.e.,  $\text{CN}^-$ ,  $\text{NO}_2^-$ ,  $\text{CO}$ ,  $\text{NH}_3$  etc. In these complexes the unpaired electrons of the central metal atom or ion are forced to pair up by strong ligands against Hund's rule. These complexes are, therefore, either diamagnetic or contain lesser number of unpaired electrons. They are also called **low spin** or **spin paired** complexes. For example,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$  are inner orbital complex ions.

**Outer orbital complexes** — The complexes which use outer  $d$ -orbitals, i.e.,  $d$  orbitals of central metal atom or ion for bond formation are called outer orbital complexes. These complexes are formed by weak ligands i.e.,  $\text{H}_2\text{O}$ ,  $\text{F}^-$ ,  $\text{Cl}^-$  etc. In these complexes, the electronic configuration of the central metal atom or ion is not disturbed. These complexes contain larger number of unpaired electrons and are also called **high spin** or **spin free** complexes. For example,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{CoF}_6]^{3-}$  are outer orbital complex ions.

These complexes are less stable than inner orbital complexes.

### • SUMMARY

- A complex ion is an electrically charged ion formed by the combination of a central metal atom or ion and a suitable number of neutral molecules or anions.
- Ligand is the neutral molecule or ion which surrounds the central metal atom or ion in a complex.
- Ligands can be monodentate, bidentate or polydentate.
- The number of covalent and coordinate bonds formed by the ligands with the central metal atom or ion is known as *coordination number*.
- The cyclic complex compounds formed when a multidentate ligand (ligand having more than one donor site) attached through two or more donor atoms to the same central metal ion are called chelate compounds.
- In coordination compounds the isomerism is due to the difference in the structure of the compounds or due to the difference in the relative arrangement of atoms or groups in space.



## 4. What are inner and outer orbital complexes ?

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## • TEST YOURSELF

- Write a note on complex salts.
- Write a note on ligand.
- What is a complex ion? Explain with examples.
- Define monodentate and bidentate ligands with suitable examples.
- What is a polydentate ligand?
- What are chelate compounds?
- Mention the distinction between chelate compounds and complex compounds.
- Define co-ordination number.
- Discuss Werner's theory of coordination compounds and its experimental verification.
- Discuss the structures of platinum amines on the basis of Werner's co-ordination theory.
- Discuss Sidwick's electronic interpretation of compounds.
- Show how the effective atomic number accounts for the stability of complexes, on the basis of Sidwick's theory?
- Write the IUPAC names of the following complexes :
 

(i) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2] \text{Cl}$	(ii) $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})] \text{Cl}_3$
(iii) $\text{H}_2[\text{PtCl}_6]$	(iv) $\text{H}_2[\text{HgI}_4]$
(v) $\text{Li}[\text{AlH}_4]$	(vi) $\text{Na}_4[\text{Ni}(\text{CN})_4]$
- Describe the different types of isomerism in co-ordination compounds with examples.
- What are the main postulates of valency bond theory?
- Discuss metal-ligand bonding of octahedral, square planar and tetrahedral complexes on the basis of VBT.
- What are the limitations of valency bond theory?
- What are inner and outer orbital complexes? Give examples of each.
- Explain why potassium ferricyanide is considered to be a complex compound, but potash alum is not?
- Explain why  $\text{NH}_4^+$  ion does not form complexes?
- Explain why geometrical isomerism is not found in tetrahedral complexes?
- Explain why optical isomerism is not found in square planar complexes?
- Haemoglobin is a coordination compound having central metal atom of :
 

(a) Ca	(b) Mg	(c) Fe	(d) Co
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- The co-ordination number of  $\text{Pt}^{4+}$  in the complex  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$  is :
 

(a) 2	(b) 4	(c) 6	(d) 8
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- The oxidation state of cobalt in  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  is :
 

(a) +2	(b) +3	(c) +4	(d) +6
--------	--------	--------	--------
- Which one of the following is used for the estimation of hardness of water :
 

(a) E.D.T.A.	(b) Dimethyl glyoxime
(c) Ethylene diamine	(d) Triphenyl phosphine
- Complex  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$  gives white precipitate with :
 

(a) $\text{AgNO}_3$	(b) $\text{BaCl}_2$	(c) KI	(d) $\text{KNO}_3$
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- Coordination number of  $\text{Co}^{3+}$  in the complex  $[\text{Co}(\text{en})_3]\text{Cl}_3$  is :
 

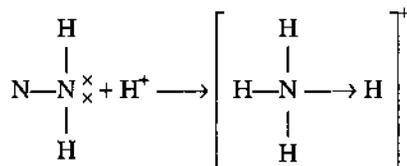
(a) 2	(b) 3	(c) 6	(d) 1
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- The effective atomic number of  $\text{Cr}^{3+}$  in  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  is :
 

(a) 32	(b) 33	(c) 34	(d) 35
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30. IUPAC name of  $K_3[Fe(CN)_6]$  is :  
 (a) Potassium hexa cyano ferrate (III)  
 (b) Potassium hexa cyano ferrate (II)  
 (c) Potassium ferrocyanide (d) Potassium iron cyanide
31. IUPAC name of  $K_2[PtCl_6]$  is :  
 (a) Potassium hexachloro platinate (II)  
 (b) Potassium hexachloro platinate (IV)  
 (c) Potassium chloroplatinate (d) Potassium platinumchloride
32. An example of hexadentate ligand is :  
 (a) 2, 2 dipyridyl (b) ethylene diamine  
 (c) ethylene diamine tetraacetate (d) imino diacetate
33. Which of the following is a complex compound ?  
 (a) Ferrous ammonium sulphate (b) Potassium ferrocyanide  
 (c) Potassium dichromate (d) Potassium aluminium sulphate
34. An example of bidentate ligand is :  
 (a)  $H_2O$  (b)  $NH_3$  (c)  $C_2O_4^{2-}$  (d)  $CN^-$
35. **Fill in the blanks**
- Ethylene diamine is an example of ..... ligand.
  - The formula of potassium trioxalate aluminate (III) is .....
  - A ligand donates at least one ..... to the metal atom or ion to form a complex.
  - In a complex compound, the primary valency of the central metal ion is satisfied by .....
  - The total number of electrons of central metal ion and those gained by ligands is called as .....
  - Dimethyl glyoxime is used for the gravimetric estimation of ..... ions.
  - The primary and secondary valency of central metal in the complex  $[Cu(NH_3)_4]SO_4$  are ..... and ..... respectively.
  - The effective atomic number of iron in  $[Fe(CN)_6]^{3-}$  ion is .....
  - IUPAC name of  $LiAlH_4$  is .....

### ANSWERS

13. (i) Tetra aquodichlorochromium (III) chloride, (ii) Pentammine aquo cobalt (III) chloride (III) Hydrogen hexachloro platinate (IV), (iv) Potassium tetraiodomercurate (II), (v) Lithium tetrahydride aluminate (III) (vi) Sodium tetracyano nickelate (0).
20. Complex formation takes place when ligand donates lone pair of electrons to the vacant orbitals of central metal ion to form coordinate bond.  $NH_4^+$  ion does not form complex compound because in this ion lone pair of electrons of nitrogen is utilized in the formation of co-ordinate bond with  $H^+$  ion and is not available for co-ordination with the central metal ion.



21. Geometrical isomerism is not found in tetrahedral complexes because in these complexes all the four ligands are at equal distance from the central metal atom.
22. Optical isomerism is not found in square planar complexes because all the four ligands are at equal distance from the central metal atom in these complexes all the four ligands and central metal atom lie in the same plane and, therefore, they contain a plane or axis of symmetry. For a compound to show optical isomerism, it is necessary that it should not have a plane or axis of symmetry..
23. (c) 24. (c) 25. (b) 26. (a) 27. (a) 28. (c) 29. (b) 30. (a) 31. (b) 32. (c) 33. (b)
34. (c) 35. (i) bidentate (ii)  $K_3[Al(C_2O_4)_3]$  (iii) electron pair (iv) anions  
 (v) effective atomic number (vi)  $Ni^{2+}$  (vii) two, four (viii) 35  
 (ix) lithium tetrahydride aluminate (III).





takes place in inner  $f$ -orbitals and as such does not affect the electronic configuration of the outermost shell, hence the properties of the members of lanthanide series possess similar characteristics. In other words, the inner transition elements are not expected to show any periodicity in their properties. Thus, a separate position of the inner transition elements outside the main part of the periodic table is justified. A few difference in properties of the lanthanide do exist which arise as a consequence of lanthanide contraction.

Lanthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Mo	Er	Tm	Yb	Lu
	58	59	60	61	62	63	64	65	66	67	68	69	70	71

### [III] Lanthanides

Lanthanum ( $\text{La}_{57}$ ) and the next fourteen elements (58 to 71) which follow it are called **lanthanides** or **lanthanons**. These fifteen elements closely resemble one another and form a separate group with lanthanum as the first member, hence the name lanthanons or lanthanides. The reason of their resemblance with lanthanum so closely lies in their electronic configurations. The configuration of lanthanum is  $[\text{Xe}] 4f^0 5d^1 6s^2$ . In the next fourteen elements, 14 electrons are added one by one to the empty  $4f$ -subshell to the lanthanum configuration. Thus, while in cerium, the element immediately following lanthanum, one  $4f$ -electron is added to the lanthanum configuration and in lutecium (Lu) the last element of the series, fourteen  $4f$ -electrons are added to the lanthanum configuration. Hence the configuration of cerium (Ce) and lutecium (Lu) are  $[\text{Xe}] 4f^1 5d^1 6s^2$  and  $[\text{Xe}] 4f^{14} 5d^1 6s^2$ , respectively. Since the number of electrons in the outermost, as well as the penultimate shell, remains the same, all the fifteen elements of the lanthanides resemble one another very closely. Strictly speaking, only 13 elements from Ce to Yb are  $f$ -block elements because in lanthanum ( $4f^0 5d^1 6s^2$ ) the  $4f$ -shell is still empty while in lutecium ( $4f^{14} 5d^1 6s^2$ ), the  $4f$ -shell is completely filled. However, all the elements from La to Lu have similar physical characteristics and hence are considered together. In fact, they are collectively named as lanthanides after lanthanum. The reason for their similar properties is same number of electrons in the  $5d$  and  $6s$  subshells and  $4f$  electrons are responsible for their difference.

### General Characteristics

(i) **Occurrence** : The lanthanides are not so scarce in the earth's crust as the name rare earths implies, potentially their sources are limited. Their substantial deposits occur in several countries, particularly in India, Scandinavia, U.S.A. and U.S.S.R. The most common occurring lanthanide is cerium which constitutes about  $3 \times 10^{-4}$  % of the earth's crust. Monazite sand is the most important mineral containing lanthanides. It is essentially a lanthanide orthophosphate. Promethium ( $\text{Pm}_{61}$ ) does not occur in nature. It has been made artificially by radioactive disintegration.

(ii) **Electronic Configuration** : The electronic configurations of lanthanides in the ground state are given in the following table. There is, however, some doubt regarding these configurations. This arises from the great complexity of the electronic spectra of these atoms. The most widely accepted electronic configuration of these elements is given.

#### Electronic configuration and oxidation states of lanthanides

Element	Electronic configuration	Oxidation states
Lanthanum,	$57\text{La} = [\text{Xe}] 4f^0 5d^1 6s^2$	+3
Cerium,	$58\text{Ce} = [\text{Xe}] 4f^1 5d^1 6s^2$	+3, +4
Praseodymium	$59\text{Pr} = [\text{Xe}] 4f^2 5d^1 6s^2$	+3, +4
Neodymium,	$60\text{Nd} = [\text{Xe}] 4f^3 5d^1 6s^2$	+2, +3, +4
Promethium,	$61\text{Pm} = [\text{Xe}] 4f^4 5d^1 6s^2$	+3
Samarium,	$62\text{Sm} = [\text{Xe}] 4f^5 5d^1 6s^2$	+2, +3
Europium,	$63\text{Eu} = [\text{Xe}] 4f^6 5d^1 6s^2$	+2, +3
Gadolinium,	$64\text{Gd} = [\text{Xe}] 4f^7 5d^1 6s^2$	+3
Terbium,	$65\text{Tb} = [\text{Xe}] 4f^8 5d^1 6s^2$	+3, +4
Dysprosium,	$66\text{Dy} = [\text{Xe}] 4f^9 5d^1 6s^2$	+3, +4
Holmium,	$67\text{Ho} = [\text{Xe}] 4f^{10} 5d^1 6s^2$	+3
Erbium,	$68\text{Er} = [\text{Xe}] 4f^{11} 5d^1 6s^2$	+3
Thullium,	$69\text{Tm} = [\text{Xe}] 4f^{12} 5d^1 6s^2$	+2, +3
Ytterbium,	$70\text{Yb} = [\text{Xe}] 4f^{13} 5d^1 6s^2$	+2, +3
Lutecium,	$71\text{Lu} = [\text{Xe}] 4f^{14} 5d^1 6s^2$	+3

(iii) **Oxidation States** : The lanthanides show variable oxidation states but much less than shown by the transition elements. All the lanthanides are in oxidation state (+3), which is very

common. Solids containing tetrapositive (+4) ions are known for a few elements but only tetrapositive cerium can be distinguished in aqueous solution. In the di-positive state (+2), the ions  $\text{Sm}^{2+}$ ,  $\text{Eu}^{2+}$  and  $\text{Yb}^{2+}$  are only known in aqueous solution. A few solid compounds of other dipositive ions have been isolated.

(i) *The (+2) state* : Only dipositive europium ( $\text{Eu}^{2+}$ ), ytterbium ( $\text{Yb}^{2+}$ ) and samarium ( $\text{Sm}^{2+}$ ) have been investigated in detail. These cations are all strong reducing agents.

(ii) *The (+3) state* : The (+3) oxidation state is the most stable for all the lanthanons except cerium. In fact, the chemistry of the lanthanons in (+3) oxidation state is the chemistry of trivalent electro +ve metals. The (+3) oxidation state corresponds to the use of the  $s^2$ -electron in the outermost shell and the  $d^1$  electron in the penultimate orbit. High lattice energy and hydration energy make (+3) oxidation state most favourable.

(iii) *The (+4) State* : Ce, Pr and Tb display (+4) oxidation state. Cerium is the only lanthanide which is stable in (+4) oxidation state.

(iv) *Oxidation potential* : The E values indicate that in acidic solution each of the lanthanides is a powerful reducing agent and yields tripositive ion readily. The couples  $\text{La(II)}-\text{La(III)}$  and  $\text{La(III)}-\text{La(II)}$  confirm that empty, half filled and completely filled  $4f$ -shells represent condition of stability.

$4f^0$ ( $\text{La}^{3+}$ )	
$4f^1$ ( $\text{Ce}^{3+}$ )	
$4f^2$ ( $\text{Pr}^{3+}$ )	
$4f^3$ ( $\text{Nd}^{3+}$ )	
$4f^4$ ( $\text{Pm}^{3+}$ )	
$4f^5$ ( $\text{Sm}^{3+}$ )	
$4f^6$ ( $\text{Eu}^{3+}$ )	
$4f^7$ ( $\text{Gd}^{3+}$ )	----- Colourless
$4f^8$ ( $\text{Tb}^{3+}$ )	----- Colourless
$4f^9$ ( $\text{Dy}^{3+}$ )	----- Colourless
$4f^{10}$ ( $\text{Ho}^{3+}$ )	----- Colourless
$4f^{11}$ ( $\text{Er}^{3+}$ )	----- Colourless
$4f^{12}$ ( $\text{Tm}^{3+}$ )	----- Colourless
$4f^{13}$ ( $\text{Yb}^{3+}$ )	----- Colourless
$4f^{14}$ ( $\text{Lu}^{3+}$ )	----- Colourless

Colour of tripositive lanthanide cations ( $\text{M}^{3+}$  ions)

(v) *Colour* : Some of the trivalent ions of lanthanides are coloured in the solid state as well as in aqueous solution. These colours are shown in table below.

The colour appears to depend upon the number of  $f$ -electrons. When their salts in the solid or solution state are exposed to light, the  $f$ -electrons of these elements absorb light from the visible region and are excited from  $f$ -orbitals of lower energy to the  $f$ -orbitals of higher energy state. Thus, the colour appears to depend upon the number of  $f$ -electrons. It has been observed that colour of the ions containing  $nf$  electrons is about the same as those containing  $(14 - n)f$  electrons. For example,  $\text{Pr}^{3+}$  and  $\text{Tm}^{3+}$  which have 2 and  $(14 - 2) = 12$  electrons in their  $f$ -subenergy level are green in colour. Moreover, the ions having empty, half completed or completed subshells are colourless.  $\text{La}^{3+}$  ( $4f^0$ ),  $\text{Gd}^{3+}$  ( $4f^7$ ) and  $\text{Lu}^{3+}$  ( $4f^{14}$ ) ions are colourless.

(vi) *Magnetic properties* : Most of the ions of lanthanide series are paramagnetic, i.e., they are attracted into the magnetic field. This is due to the presence of unpaired  $f$ -electrons in these ions.  $\text{La}^{3+}$  ( $4f^0$ ),  $\text{Ce}^{4+}$  ( $4f^0$ ) and  $\text{Lu}^{3+}$  ( $4f^{14}$ ) are diamagnetic and are repelled by the magnetic field.

In these elements  $4f$  orbitals are deep inside the metal ion and are well shielded from the surroundings by  $5s$  and  $5p$  subshells. It is, therefore, not possible to explain their magnetic moments in terms of number of unpaired electrons alone. The magnetic moment can be calculated by using the equation :

$$\mu = \sqrt{4S(S+1) + L(L+1)}$$

where  $\mu$  is the magnetic moment in Bohr Magnetons (B.M.) calculated by using both the spins and orbital momentum contribution.  $S$  is the resultant spin quantum number and  $L$  is the resultant orbital momentum quantum number.

(vii) *Isotopes* : The number of naturally occurring isotopes show a regular variation. Elements with even atomic number are more stable, more abundant and exist in the form of larger number of isotopes in comparison to those with odd atomic number. Elements with odd atomic number have at the most two isotopes as seen from the following table.

## Isotopes of lanthanides

Element	Atomic No.	No. of Isotopes
Ce	58	4
Pr	59	1
Nd	60	7
Pm	61	0
Sm	62	7
Eu	63	2
Gd	64	7
Tb	65	1
Dy	66	7
Ho	67	1
Er	68	6
Tm	69	1
Yb	70	7
Lu	71	2

**(viii) Basic character :** They form ionic and basic hydroxides of the general formula  $M(OH)_3$ . They are stronger bases than  $Al(OH)_3$  but weaker than  $Ca(OH)_2$ . The basic character of these hydroxides decreases as the atomic number increases.

**(ix) Solubility of compounds :** Salts of lanthanides are generally hydrated. Their solubility follows the pattern of solubility of salts of group II A elements. Chlorides, bromides, iodides, nitrates, acetates, perchlorates and bromates are generally water soluble while fluorides, hydroxides, oxides and salts of most *di-* and *tri-*negative anions (e.g.  $CO_3^{2-}$ ,  $CrO_4^{2-}$ ,  $PO_4^{3-}$ ,  $C_2O_4^{2-}$ ) are generally insoluble. The sulphates are, however, soluble unlike group II.

**(x) Double salts :** Lanthanides form double salts in many cases. The important double salts are :

- (i) Carbonates e.g.  $K_2CO_3 \cdot Ce_2(CO_3)_3 \cdot 3H_2O$
- (ii) Nitrates e.g.  $3Mg(NO_3)_2 \cdot 2R(NO_3)_3 \cdot 24H_2O$
- (iii) Sulphates e.g.  $(NH_4)_2SO_4 \cdot R_2(SO_4)_3 \cdot 8H_2O$

where R stands for lanthanide element.

**(xi) Chemical reactivity :** They are very reactive metals. On burning in air, they form oxides of the general formula  $M_2O_3$  except cerium which forms  $CeO_2$ . They react with hydrogen, carbon, silicon, nitrogen, sulphur and halogens to form corresponding compounds. They decompose water to give hydrogen.

**(xii) Formation of complex compounds :** They form complex compounds but their tendency to form complexes is less than transition metal ions. The lanthanide ions in spite of high charge have low charge density because of their large size. Some of the stable complexes formed by lanthanons are well known. The examples are halo complexes  $[MF]^{++}$ , sulphito complexes  $[MSO_3]^+$ , sulphato complexes  $[MSO_4]^+$ , thiosulphato complexes  $[MS_2O_3]^+$  and oxalato complexes  $[M(C_2O_4)]^+$ . They form stable complexes with chelating ligands such as E.D.T.A., oximes and  $\beta$ -ketones. The tendency to form complexes and their stability increases with increase in the atomic number.

**(xiii) Density :** The density depends upon the atomic weight, atomic radius and the structure of the aggregate. It is a general trend in a periodic family that density increases with increase in atomic weight. This trend is observed in lanthanides also. The reason is that the increase in atomic weights in lanthanides is comparatively larger than the increase in volumes of individual atoms, since the lanthanides have almost the same atomic radii. The exceptions are europium (Eu) and ytterbium (Yb).

**(xiv) Melting and boiling points :** The low and high melting points are determined by the magnitude of the attractive forces holding the component particles all together in the crystalline state. It is an important feature to note rapid upward trend in melting points, among the elements of almost similar size. The exceptions are at europium (Eu) and ytterbium (Yb). The much low m. pt. of these two elements are in accordance with their metallic radius and divalency. The divalency indicates that less number of electrons per atom are available to form metallic bonding in comparison with other lanthanides.

Unlike the trend in melting points, the large upward trend in boiling points is no longer present. Again, the low boiling points of europium and ytterbium are due to weak metallic bonding in them.

**(xv) Ionization potential :** In the inner transition series, the values of first ionization potentials are almost constant. This is because the addition of an electron to an inner quantum shell gives a high shielding effect which virtually compensates the increased nuclear charge.

## • 8.2. LANTHANIDE CONTRACTION

There is a general increase in radii of atoms and ions of scandium, yttrium and lanthanum with increase in atomic number. This is because the addition of electrons to higher energy levels overcomes increasing contractive effect produced by increased nuclear charge. However the situation is entirely different in lanthanides. In lanthanides, there is a regular decrease in radii of the atoms and ions. This is known as **lanthanide contraction**.

**Cause of lanthanide contraction :** The electronic configuration of these elements shows that in these elements the differentiating electron enters in the *f* subenergy level and not in the valency shell. The screening effect of *f*-electrons is very small. On the other hand, nuclear charge increases with the increase in the atomic number. Due to less screening effect, the *f*-electrons cannot reduce the effect of nuclear charge to that extent. As a result, the valency electrons are attracted by the nucleus with a greater force and therefore, atomic and ionic radii decrease with the increase in the atomic number.

La <sup>3+</sup>	Ce <sup>3+</sup>	Pr <sup>3+</sup>	Nd <sup>3+</sup>	Pm <sup>3+</sup>	Sm <sup>3+</sup>	Eu <sup>3+</sup>	Gd <sup>3+</sup>	Tb <sup>3+</sup>	Dy <sup>3+</sup>
1.15	1.11	1.09	1.08	1.06	1.04	—	1.02	1.00	0.99
Ho <sup>3+</sup>	Er <sup>3+</sup>	Tm <sup>3+</sup>	Yb <sup>3+</sup>	Lu <sup>3+</sup>					
0.97	0.96	0.95	0.94	0.93					

Ionic radii of lanthanides

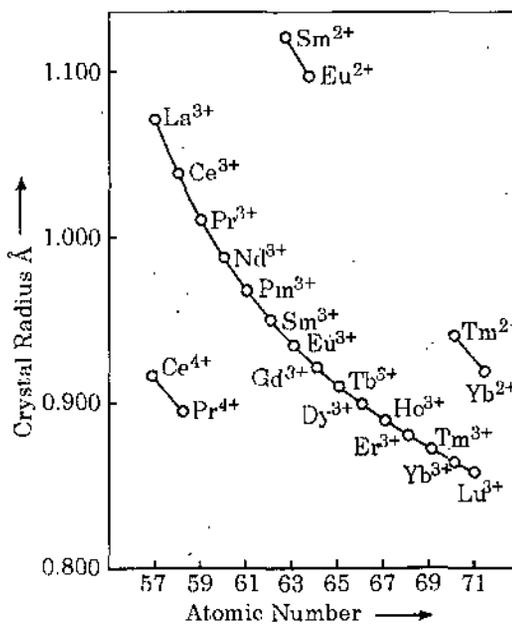


Fig. 1. Crystal radii of La<sup>3+</sup>, Gd<sup>3+</sup> and Lu<sup>3+</sup> ions as a function of their atomic number.

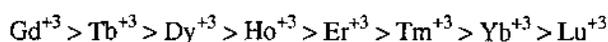
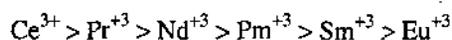
**Consequences of lanthanide contraction :** Lanthanide contraction has a significant effect on the relative properties of elements which come before and after the lanthanides in the periodic table. Some of these effects are given below :

**(a) The position of yttrium :** The magnitude of the lanthanide contraction results in the position of Y<sup>+3</sup> (ionic radius 0.98 Å) between Dy<sup>+3</sup> (ionic radius 0.99) and Ho<sup>+3</sup> (ionic radius 0.97). The similarity in ionic radii of Y<sup>+3</sup> with that of the heavier lanthanides and the similarities in crystal structure, solubility and chemical properties of the yttrium compounds with those of the heavier lanthanides. These facts make yttrium a practical member of the lanthanide series.

## Atomic radii of elements preceding lanthanides

Y <sub>39</sub>	Zr <sub>40</sub>	Nb <sub>41</sub>	Mo <sub>42</sub>	Tc <sub>43</sub>	Ru <sub>44</sub>	Rh <sub>45</sub>	Pd <sub>46</sub>
1.62	1.45	1.34	1.29	...	1.24	1.25	1.28
La* <sub>57</sub>	Hf <sub>72</sub>	Ta <sub>73</sub>	W <sub>74</sub>	Re <sub>75</sub>	Os <sub>76</sub>	Ir <sub>77</sub>	Pt <sub>78</sub>
1.69	1.44	1.34	1.30	1.28	1.26	1.26	1.26
La.....Lu <sub>71</sub> (Lanthanides)							

**(b) Similarity among lanthanides :** Due to lanthanide contraction, lanthanons show a lot of resemblance. The lanthanide contraction resulted in slight differences in the physical properties among the lanthanides themselves which enabled the separation of the lanthanides by fractional means. The lanthanide contraction also explains the decreasing basicity of the lanthanides (La—Lu) since according to Fajan's rule the larger the cation the more will be the tendency of its hydroxide to dissociate and thus La having the largest ionic radius is the most basic, while Lu having the lowest ionic radius is the least basic, the yttrium falls in the middle of the lanthanide series. The basicity is expected to decrease in the order.



**(c) Similar atomic radii and similar properties of the elements of second and third transition series :** We know that atomic radius increases in a group as the atomic number increases. Consequently the atomic radius increases from scandium (Sc) to yttrium (Y) to lanthanum (La). Similarly, we expect normal increase in size in other groups :

21Sc	22Ti	23V	24Cr
39Y	40Zr	41Nb	42Mo
57La	72Hf	73Ta	74W

However, after the lanthanides, the increase in the size from second and third transition series is not observed. The pairs of elements Zr—Hf, Nb—Ta, Mo—W etc. possess almost the same size. The properties of these elements are also very similar.

Zr	Nb	Mo
1.45 Å	1.34 Å	1.29 Å
Hf	Ta	W
1.44 Å	1.34 Å	1.30 Å

As a result of lanthanide contraction the elements of second and third transition series resemble each other much more than the elements of first and second transition series.

**(d) Densities :** The densities of second series of transition elements are only slightly higher than those of first series while the densities of third series of these elements are nearly two times the densities of corresponding elements in second transition series.

**(e) Hardness, melting point and boiling point :** The hardness, melting point and boiling point of some elements after atomic number 72 (Hf) are higher than expected due to lanthanide contraction. This is because the attraction between the atoms increases as the size decreases.

**(f) Ionization potential :** We know that ionization potential decreases in a group as the atomic number increases. However, the ionization potential of the elements from atomic number 73 (Ta) to 80 (Hg) in *d*-block and 81 (Tl), 82 (Pb) in *p*-block elements are higher than those of the elements of the same group above them. This abnormal behaviour is due to lanthanide contraction.

### • 8.3. SEPARATION OF LANTHANIDES

The properties of metal ions are determined by their charge and size. Since all the lanthanides have the same charge and are of same size, they have almost same properties. Hence, the separation of lanthanides from one another is very difficult. The different methods used for their separation are based on the slight differences of properties like stability, solubility, complex formation, basic properties etc. The modern methods used for their separation are as follows :

**(1) Valency change method :** The most common oxidation state of lanthanides is +3. In addition to this, some of the lanthanides also show +2 and +4 oxidation states. The properties of

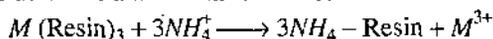
lanthanide ions in +2 and +4 oxidation states are different from those of the ions in +3 oxidation state. This is taken as the basis of their separation. For example, cerium is separated from other lanthanides by its oxidation with alkaline  $\text{KMnO}_4$  to  $\text{Ce}^{4+}$ . This is less basic and is precipitated as a basic salt,  $\text{Ce}(\text{OH})_4 \cdot \text{CeO}_2$ . The trivalent ions of other lanthanides remain in solution.

Similarly, europium can be separated from a mixture of trivalent lanthanides by reducing it to +2 state by  $\text{Zn/Hg}$ .  $\text{Eu}^{2+}$  can be precipitated as  $\text{EuSO}_4$ . The sulphates of all other trivalent lanthanides remain in solution.

**(2) Ion exchange method :** This is the most rapid and effective method for the separation of lanthanides. For this a column of synthetic ion exchange resin with acidic functional groups ( $-\text{SO}_3\text{H}$  or  $-\text{COOH}$ ) is used. The solution of mixture of lanthanide ions is allowed to flow through the column when hydrogen ions are replaced by the metal ions.



The column now contains the lanthanide ions fixed on the resin. The column is now eluted with citric acid and ammonium citrate solution. The ammonium ions replace the lanthanide ions.



It has been observed that the ions which are bound loosely to the resin are displaced by the  $\text{NH}_4^+$  ions first while those which are bound most firmly are displaced in the last. The firmness with which lanthanide ions are bound to the resin decreases from  $\text{La}^{3+}$  to  $\text{Lu}^{3+}$ . Thus,  $\text{Lu}^{3+}$  ion is eluted first while  $\text{La}^{3+}$  ion is eluted in the last.

## • 8.4. CHEMISTRY OF ACTINIDES

### [I] Introduction

Actinium ( $_{89}\text{Ac}$ ) and the next fourteen elements (90 to 103) which follow it are called **actinides** or **actinons**. These fifteen elements closely resemble one another and form a separate group with actinium as the first member, hence the name actinides or actinons. The reason of their resemblance with actinium so closely lies in their electronic configurations. The electronic configuration of actinium is  $[\text{Rn}] 5f^0 6d^1 7s^2$ . In the next fourteen elements, 14 electrons are added one by one to the empty  $5f$  subshell to the actinium configuration. Thus, the configuration of thorium ( $_{90}\text{Th}$ ) and lawrencium ( $_{103}\text{Lw}$ ) are  $[\text{Rn}] 5f^1 6d^1 7s^2$  and  $[\text{Rn}] 5f^{14} 6d^1 7s^2$ . Since the number of electrons in the outermost as well as penultimate shell remains the same, all the fifteen elements of the actinides resemble one another very closely. **The elements after uranium are called transuranic elements.** These are all synthetic elements and are the result of atomic research. The main characteristics of these elements are :

### [II] General Characteristics of Actinides

**(i) Electronic configuration :** The electronic configuration of two outermost shells of these elements remains the same and the differentiating electron enters in the  $5f$ -subenergy level. *The electronic configurations of actinides are also uncertain. This is because the energies of  $5f$  and  $6d$  subshells are almost equal and sometimes it is difficult to ascertain whether the differentiating electron enters into  $5f$  or  $6d$  subenergy level. The most widely accepted electronic configuration of these elements is given in the following table.*

Element	Electronic configuration	Oxidation states
Actinium,	$_{89}\text{Ac} = [\text{Rn}] 5f^0 6d^1 7s^2$	+3
Thorium,	$_{90}\text{Th} = [\text{Rn}] 5f^1 6d^1 7s^2$	(+3), +4
Protactinium,	$_{91}\text{Pa} = [\text{Rn}] 5f^2 6d^1 7s^2$	(+3), +4, +5
Uranium	$_{92}\text{U} = [\text{Rn}] 5f^3 6d^1 7s^2$	+2, +3, +4, +5, +6
Neptunium,	$_{93}\text{Np} = [\text{Rn}] 5f^4 6d^1 7s^2$	+3, +4, +5, +6, +7
Plutonium,	$_{94}\text{Pu} = [\text{Rn}] 5f^5 6d^1 7s^2$	+3, +4, +5, +6, +7
Americium,	$_{95}\text{Am} = [\text{Rn}] 5f^7 6d^0 7s^2$	+2, +3, (+4), +5, +6
Curium,	$_{96}\text{Cm} = [\text{Rn}] 5f^7 6d^1 7s^2$	+3, (+4)
Berkelium,	$_{97}\text{Bk} = [\text{Rn}] 5f^8 6d^1 7s^2$	+3, +4
Californium,	$_{98}\text{Cf} = [\text{Rn}] 5f^9 6d^1 7s^2$	(+2), +3
Einsteinium,	$_{99}\text{Es} = [\text{Rn}] 5f^{10} 6d^1 7s^2$	(+2), +3
Fermium,	$_{100}\text{Fm} = [\text{Rn}] 5f^{11} 6d^1 7s^2$	+2, +3
Mendelevium,	$_{101}\text{Md} = [\text{Rn}] 5f^{12} 6d^1 7s^2$	(+2), +3
Nobelium,	$_{102}\text{No} = [\text{Rn}] 5f^{13} 6d^1 7s^2$	+2, +3
Lawrencium,	$_{103}\text{Lw} = [\text{Rn}] 5f^{14} 6d^1 7s^2$	+3

The change in the electronic configuration of americium is due to the stability associated with half completed  $f$ -subshells.

**(ii) Oxidation states** : They show variable oxidation states. The most important oxidation state of these elements is +3 and their stability increases with the increase in the atomic number. The different oxidation states of these elements are shown in the above table. The unstable oxidation states are shown in bracket.

**(iii) Atomic and ionic radii (Actinide contraction)** : The atomic and ionic radii of these elements decrease with the increase in the atomic number. It has been observed that on going from  $\text{Ac}^{3+}$  to  $\text{Cm}^{3+}$ , the ionic radius decrease from 1.11 Å to 0.98 Å. This regular decrease of atomic and ionic radius is known as *actinide contraction*. The electronic configuration of these elements shows that in these elements, the differentiating electron enters in the  $f$ -subenergy level and not in the valency shell. The screening effect of  $f$ -electrons is very small. On the other hand, nuclear charge increases with the increase in the atomic number. Due to less screening effect, the  $f$ -electrons can not reduce the effect of nuclear charge to that extent. As a result, the valency electrons are attracted by the nucleus with a greater force and therefore, atomic and ionic radii decrease with the increase in the atomic number.

**(iv) Formation of coloured salts** : They form coloured salts. The colour appears to depend upon the number of  $5f$  electrons. When their salts in the solid or solution state are exposed to light, the  $f$ -electrons of these elements absorb light from the visible region and are excited from  $f$ -orbitals of lower energy state to the  $f$ -orbitals of higher energy state. It has been observed that the ions having empty, half completed or completed  $f$ -subshells are colourless. For example,  $\text{Ac}^{3+}$  ( $5f^0$ ) is colourless,  $\text{U}^{3+}$  ( $5f^3$ ) is red in colour.

**(v) Formation of complex compounds** : They form complex compounds and their tendency to form complex compounds is greater than lanthanides. Most of the actinide halides form complexes with alkali metal halides, for example,  $\text{ThCl}_4$  reacts with  $\text{KCl}$  to form complexes  $\text{KThCl}_5$ ,  $\text{K}_2\text{ThCl}_6$ . Thorium tetrachloride also forms complexes with pyridine, E.D.T.A. and oxine.

**(vi) Magnetic properties** : Most of the ions of actinide series are paramagnetic, *i.e.*, they are attracted into the magnetic field. This is due to the presence of unpaired  $f$ -electrons in these ions.  $\text{Ac}^{3+}$  ( $5f^0$ ),  $\text{Th}^{4+}$  ( $5f^0$ ) and  $\text{Lw}^{3+}$  ( $5f^{14}$ ) are diamagnetic and are repelled by the magnetic field.

In these elements  $5f$  orbitals are deep inside the metal ion and are well shielded from the surroundings by  $6s$  and  $6p$  subshells. It is, therefore, not possible to explain their magnetic moments in terms of number of unpaired electrons alone. The magnetic moment can be calculated by using the equation :

$$\mu = \sqrt{4S(S+1) + L(L+1)}$$

where  $\mu$  is the magnetic moment in Bohr Magnetons (B.M.) calculated by using both the spins and orbital momentum contribution.  $S$  is the resultant spin quantum number and  $L$  is the resultant orbital momentum quantum number.

**(vii) Chemical reactivity** : They are reactive metals and react with hydrogen, oxygen, halogens and acids.

### [III] Similarity between Lanthanides and Actinides :

(1) In both the series, there is a regular filling of  $f$ -subenergy levels of their electronic configuration.

(2) Both show a common oxidation state of +3.

(3) Both are electropositive and have high chemical reactivity.

(4) There is a decrease in the atomic and ionic sizes (lanthanide and actinide contraction) in both the series with increase in the atomic number.

(5) The lanthanides and actinides having same number of unpaired electrons have quite similar spectra. The sharp line like bands appear due to  $f-f$  transitions in both the series.

(6) The nitrates, sulphates and perchlorates of trivalent lanthanides and actinides are soluble in water whereas their carbonates, hydroxides and fluorides are insoluble.

### [IV] Difference Between Lanthanides and Actinides

	Lanthanides	Actinides
1.	Except promethium they are non-radioactive.	They are all radioactive.
2.	The lanthanides show less number of oxidation states. In addition to most common oxidation state +3, few of them also show +2 and +4 oxidation states.	The actinides show greater number of oxidation states. In addition to most common oxidation state +3, they also show +2, +4, +5, +6 and +7 oxidation states.

3.	In lanthanides, 4f electrons have greater screening effect. The decrease in their ionic sizes is less.	In actinides, 5f electrons have lesser screening effect. The decrease in their ionic sizes is more.
4.	The binding energies of 4f electrons are higher.	The binding energies of 5f electrons are less.
5.	They have lesser tendency to form complex compounds.	They have greater tendency to form complex compounds.
6.	Their compounds are less basic.	Their compounds are more basic.
7.	They do not form oxo-ions.	They form oxo ions such as $\text{UO}_2^{2+}$ , $\text{PuO}_2^+$ etc.

### • 8.5. URANIUM

Uranium was discovered by Klaproth in 1789 in the mineral pitch blende and its radioactive character was first of all discovered by Becquerel in 1895.

**Occurrence** : Uranium is widely distributed in a variety of rocks and in the sea water. In the combined state, it occurs in a few rare minerals. All uranium minerals are radioactive. The chief minerals are :

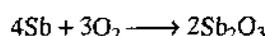
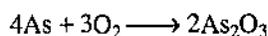
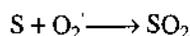
- (i) **Pitch blende**— $\text{U}_3\text{O}_8$  : It contains 75–95% of  $\text{U}_3\text{O}_8$ .
- (ii) **Carnotite**— $\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  : It contains 61–67% of  $\text{U}_3\text{O}_8$ .
- (iii) **Uranite**— $(\text{UO}_2)_2(\text{VO}_3)_2 \cdot 15\text{H}_2\text{O}$  : It contains 75–95% of  $\text{U}_3\text{O}_8$ .
- (iv) **Clevite**— $\text{U}_3\text{O}_8$  : It contains 57–72% of  $\text{U}_3\text{O}_8$ .

In India, uranium occurs in monazite sand of Kerala state. Some deposits of uranium are found in Bihar, Bengal, Madras and Gaya district.

**Extraction** : The most important ore from which uranium is extracted is pitch blende which in addition to uranium also contains Ra, Pb, Ba, Ag, Cu, S, As, Sb etc. The extraction of the metal from pitch blende involves the following steps :

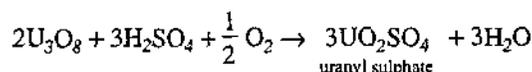
(1) **Preparation of  $\text{U}_3\text{O}_8$**  : (i) The ore is concentrated by gravity process, i.e., it is washed with rapidly flowing current of water when lighter impurities are washed away leaving behind heavier particles of the ore.

(ii) The concentrated ore is roasted in the reverberatory furnace when S, As and Sb are removed as their volatile oxides.

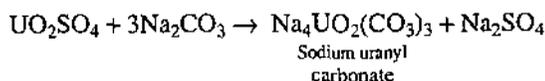


(iii) The roasted ore is treated with NaCl at  $800^\circ\text{C}$  to remove silver as insoluble silver chloride.

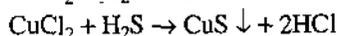
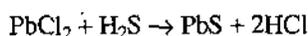
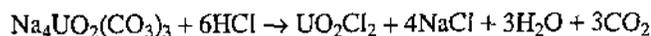
(iv) Now the resulting product is treated with dil.  $\text{H}_2\text{SO}_4$  in the presence of an oxidizing agent,  $\text{MnO}_2$ , when Ra, Pb and Ba are precipitated as sulphates and uranium goes into solution as uranyl sulphate.



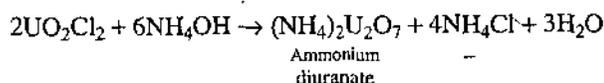
The uranyl sulphate so obtained is treated with  $\text{Na}_2\text{CO}_3$  when sodium uranyl carbonate is obtained.

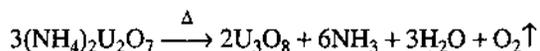


(v) The solution of sodium uranyl carbonate is acidified with conc. HCl and  $\text{H}_2\text{S}$  gas is passed through the solution when Pb and Cu are precipitated as their sulphides and solution of uranyl chloride is obtained.

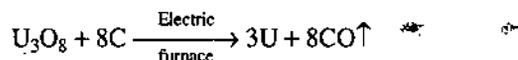


(vi) The solution of uranyl chloride is treated with excess of  $\text{NH}_4\text{OH}$  when ammonium diuranate is obtained which on heating gives  $\text{U}_3\text{O}_8$ .





(2) Reduction of  $\text{U}_3\text{O}_8$  : (i) By carbon :



(ii) By aluminothermic process : Pure uranium is best prepared by reducing the oxide by aluminium powder. The  $\text{U}_3\text{O}_8$  is mixed with equal amount of aluminium powder. The mixture is called thermite. It is now kept in a cavity made in a packing of fluorspar or sand in a tin. A small starter containing 15 parts  $\text{BaO}_2$  and 2 parts Mg powder is immersed under the thermite. The starter is connected with an Mg wire. The Mg wire is ignited at the outer end. Soon the flame reaches the starter and the whole mass bursts into flame. The metal oxide is reduced to the metal. The metal is obtained in molten state due to the large amount of heat produced during the reaction. Fluorspar or sand saves the loss of heat by radiation.

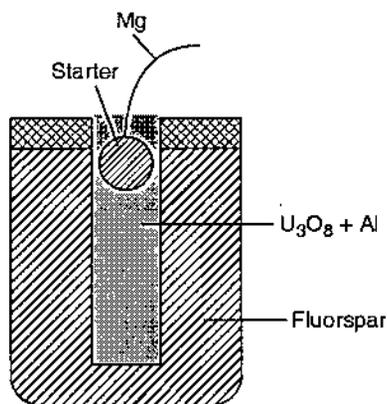
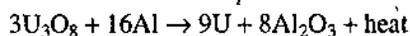
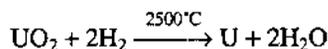
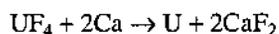
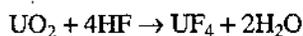


Fig. 2. Reduction of oxide by aluminothermic process.

(iii) By hydrogen :



Uranium dioxide obtained above may also be reduced to the metal by converting into uranium tetrafluoride and then reducing it by heating with calcium or magnesium metal.



Uses : (1) The most important use of uranium is in the production of nuclear energy. The energy produced by the fission of  $\text{U}^{235}$  is utilized for running power plants.

(2) The metallic uranium and its carbide are one of the best catalysts in the Haber's process for the manufacture of  $\text{NH}_3$ .

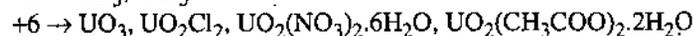
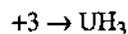
(3) Uranium compounds are used as mordants for silk and wool.

(4) Uranium compounds are used in ceramics to produce coloured glasses like yellow, orange, green or black.

(5) Uranyl nitrate is used as a reagent for the estimation of phosphates and arsenates. Uranyl acetate is used in micro analysis of sodium.

(6) Uranium is used for making special steels. Uranium-copper alloy has high conductivity and is resistant to corrosion.

**Compounds in Each Oxidation State of Uranium :** The possible oxidation states of uranium are +2, +3, +4, +5 and +6. Some compounds in these oxidation states are :







18. Which of the following has a stable +4 oxidation state ?  
 (a) La (b) Eu (c) Gd (d) Ce
19. Which lanthanide is commonly used :  
 (a) La (b) Nb (c) Th (d) Ce
20. The electronic configuration of gadolinium (At. no. = 64) is :  
 (a)  $[\text{Xe}] 4f^0 5d^8 6s^2$  (b)  $[\text{Xe}] 4f^7 5d^1 6s^2$   
 (c)  $[\text{Xe}] 4f^3 5d^5 6s^2$  (d)  $[\text{Xe}] 4f^6 5d^2 6s^2$
21. The lanthanide contraction is responsible for the fact :  
 (a) Zr and Y have about the same radius  
 (b) Zr and Hf have about the same radius  
 (c) Zr and Zn have the same oxidation state  
 (d) Zr and Nb have the same oxidation state
22. In which class of elements, there is a regular filling of 5f sub energy level ?  
 (a) Actinides (b) Lanthanides  
 (c) Transition elements (d) Coinage metals
23. Which of the following elements does not belong to actinides ?  
 (a) Cm (b) Pu (c) Ce (d) Th
24. All the actinides exhibit a valency of :  
 (a) 2 (b) 3 (c) 4 (d) 6
25. **Fill in the blanks :**  
 (i) Lanthanides are characterized by the regular filling of ..... subenergy level of their electronic configuration.  
 (ii) The most common oxidation state of lanthanides is .....  
 (iii) The outer electronic configuration of lanthanum (At. No. 57) is .....  
 (iv) Lanthanides are also called ..... elements.  
 (v) The most important ore of uranium is .....  
 (vi) The elements after uranium are called ..... elements.

### ANSWERS

16. (d) 17. (a) 18. (d) 19. (d) 20. (b) 21. (b) 22. (a) 23. (c) 24. (b)  
 25. (i) 4f (ii) +3 (iii)  $[\text{Xe}] 4f^0 5d^1 6s^2$   
 (iv) rare earth (v) Pitch blende (vi) transuranic



## 9

GENERAL METHODS OF EXTRACTION,  
PURIFICATION OF METALS AND  
METALLURGY

## STRUCTURE

- General Methods of Extraction and Purification of Metals
- Metallurgy of Titanium
- Metallurgy of Vanadium
- Metallurgy of Chromium
- Metallurgy of Nickel
- Metallurgy of Platinum
  - Summary
  - Student Activity
  - Test Yourself

## LEARNING OBJECTIVES

After going through this unit you will learn :

- Minerals and area.
- Electromagnetic method and Froth floatation process
- Acid process, chlorine process and Wohler's process.
- Mond's process
- German silver, monel metal, cupro nickel, nichrome and nickel steel.
- Bredig's arc method
- Different forms of platinum

### • 9.1. GENERAL METHODS OF EXTRACTION AND PURIFICATION OF METALS

#### [I] Minerals and Ores

The metals can be found in nature either in free or in the combined state. The metals, e.g., Au, Pt, Ag, Hg which do not react with oxygen,  $\text{CO}_2$ , moisture etc. occur in the free state, whereas others which react with them are found in the combined state. *The compounds of metals which occur in nature along with earthy impurities are called as minerals and minerals from which the metals can be obtained conveniently and economically are called as ores.* The metals in the combined state occur mainly as oxides, sulphides, carbonates, halides and sulphates.

(i) **Oxides** : The metals like aluminium, iron, zinc, tin, manganese occur as oxides, e.g. bauxite ( $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ), haematite ( $\text{Fe}_2\text{O}_3$ ), zincite ( $\text{ZnO}$ ), cassiterite ( $\text{SnO}_2$ ), pyrolusite ( $\text{MnO}_2$ ) and so on.

(ii) **Sulphides** : The metals like lead, copper, silver, zinc, mercury, etc. occur as sulphides, e.g., galena ( $\text{PbS}$ ), copper pyrites ( $\text{CuFeS}_2$ ), argentite ( $\text{Ag}_2\text{S}$ ), zinc blende ( $\text{ZnS}$ ), cinnabar ( $\text{HgS}$ ).

(iii) **Carbonates** : The metals like calcium, magnesium, copper, iron zinc occur as carbonates, e.g., lime stone ( $\text{CaCO}_3$ ), magnesite ( $\text{MgCO}_3$ ), malachite [ $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$ ], siderite ( $\text{FeCO}_3$ ), Calamine ( $\text{ZnCO}_3$ ).

(iv) **Halides** : The metals like sodium, potassium, calcium, magnesium, aluminium, silver occur as halides, e.g., common salt ( $\text{NaCl}$ ), carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), fluorspar ( $\text{CaF}_2$ ), cryolite ( $\text{Na}_3\text{AlF}_6$ ), horn silver ( $\text{AgCl}$ ).

(v) **Sulphates** : The metals like sodium, magnesium, lead, barium, calcium occur as sulphates, e.g., Glauber's salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), Epsom salt ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), anglesite ( $\text{PbSO}_4$ ), barytes ( $\text{BaSO}_4$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).

## [(II)] Metallurgy

The chemistry of the extraction of metals from their ores is known as metallurgy. The extraction of metals involves individual procedure and the line of treatment depends upon the nature of the ore and properties of the metal. Some common steps used in the extraction of metals are :

(i) **Crushing of ore** : The big lumps of ores are broken to smaller pieces by hammering or by means of mechanical crushers. It is now powdered by means of a battery of stamp mills.

(ii) **Concentration** : The process of removal of earthy impurities from the ore is known as concentration. The ore is concentrated by the following methods depending upon the nature of the ore.

(i) **Gravity method** : The method is used when there is a large difference in the specific gravities of ore and the earthy impurities. The finely powdered ore is washed with a rapidly flowing current of water when lighter impurities are washed away leaving behind heavier particles of the ore. The oxide ores are generally concentrated by this process, e.g., chromite ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ), pyrolusite ( $\text{MnO}_2$ ) etc.

(ii) **Electromagnetic method** : The method is used if some of the impurities of the ore are magnetic in nature. The finely powdered ore is dropped over the belt moving over the electromagnetic rollers. The magnetic material is attracted by the magnetic roller and falls near to the

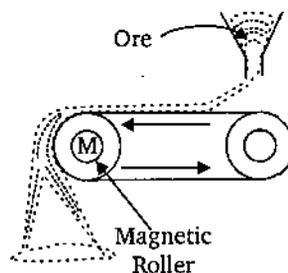


Fig. 1. Concentration of the ore by electromagnetic method

roller, whereas other part falls a distance far off. For example, cassiterite ( $\text{SnO}_2$ ) containing magnetic impurity wolframite ( $\text{FeWO}_4$ ) is concentrated by this method.

(iii) **Froth floatation process** : The sulphide ores are concentrated by this process as they are easily wetted by oils. The finely powdered ore is mixed with water, some pine oil and air is passed through it. The ore particles are easily wetted by the oil and come to the surface in the form of froth, whereas earthy impurities sink to the bottom.

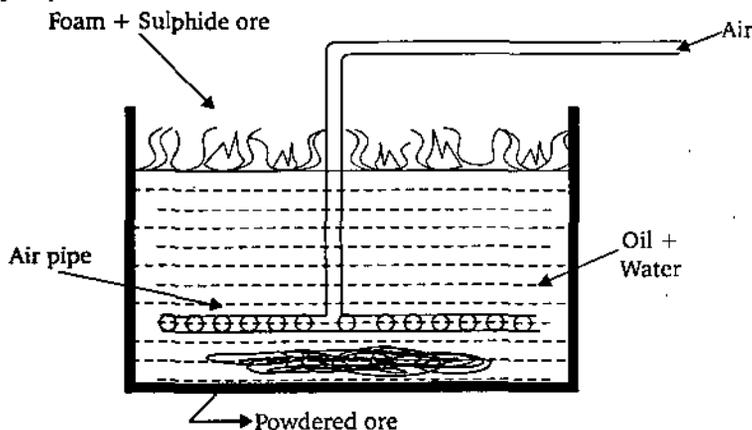


Fig. 2. Froth floatation process for the concentration of sulphide ores.

The sulphide ores like galena, copper pyrites ( $\text{CuFeS}_2$ ), cinnabar ( $\text{HgS}$ ) are concentrated by this process.

**Preparation of oxide : (i) Roasting :**  
It is a process of heating the ore strongly in the presence of excess of air in a reverberatory furnace when volatile impurities are removed and the ore is partially or completely changed to oxide. The process is generally used for sulphide ores. By roasting sulphur and arsenic present in the ore are volatilized off as their oxides.

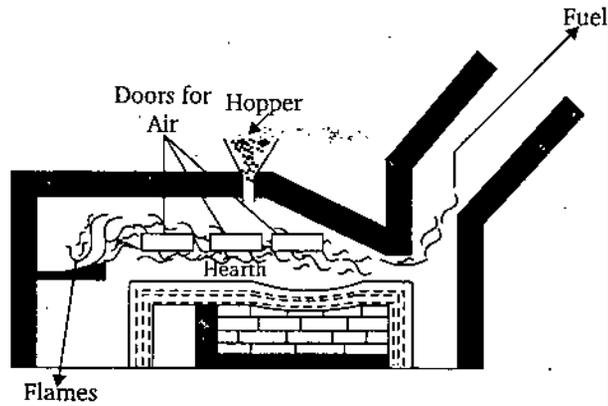
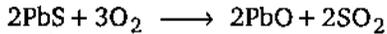
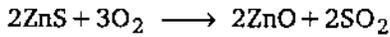
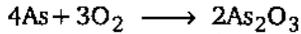
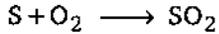
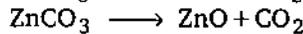
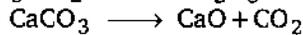
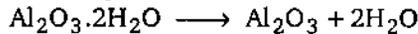


Fig. 3. Roasting of ore by reverberatory furnace.

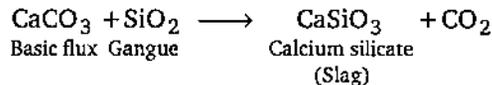


**(ii) Calcination :** It is a process of heating the ore strongly in the absence of air to remove moisture,  $CO_2$  and other volatile impurities.

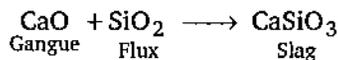


The calcined ore becomes porous and thus, can be easily reduced.

**(iii) Smelting :** The process in which finely powdered ore is heated with coke and flux at a high temperature so as to obtain the metal in the fused state is known as smelting. A flux is a substance which combines with the gangue to form easily fusible slag. The slag being lighter than the molten metal comes to the surface and is easily removed. The flux used may be acidic or basic depending upon the nature of impurity. For example, basic flux such as limestone or magnesite is used when the gangue is sand (acidic).



Similarly, an acidic flux such as silica is used when the gangue is basic containing metallic oxides.

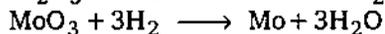


**Reduction to the free metal :** The roasted or calcined ore is then reduced to the free metal. The reduction may be done by the following processes :

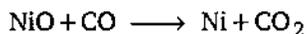
**(i) By carbon :** The oxides of less electropositive metals like lead, zinc, tin are reduced by strongly heating with coal or coke.



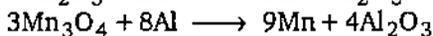
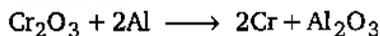
**(ii) By carbon monoxide or hydrogen :** The oxides of some metals may also be reduced by carbon monoxide or hydrogen.



Water gas is also used for the reduction of NiO.



**(iii) By aluminothermic process :** The oxides of metals which remain unaffected by carbon are reduced by aluminium.



The metal oxide is mixed with equal amount of aluminium powder. The mixture is called as **thermite**. It is now kept in a cavity made in a packing of flourspar or sand in a tin. A small starter containing 15

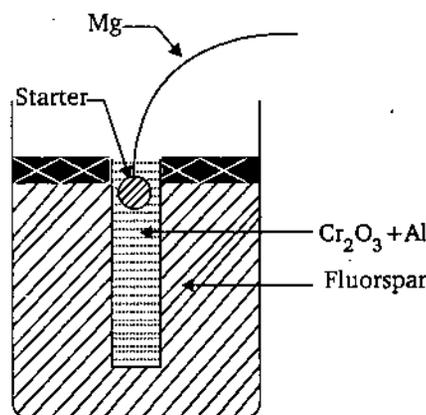
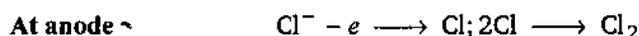


Fig. 4. Reduction of oxide by aluminothermic process.

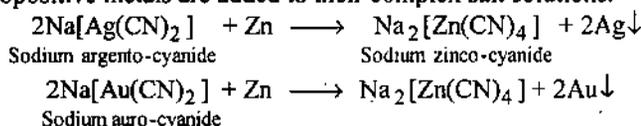
parts  $\text{BaO}_2$  and 2 parts Mg powder is immersed under the thermite. The starter is connected with a Mg wire. The Mg wire is ignited at the outer end. Soon the flame reaches to the starter and the whole mass bursts into flame. The metal oxide is reduced to the metal. The metal is obtained in molten state due to the large amount of heat produced during the reaction. Fluorspar or sand saves the loss of heat by radiation.

(iv) **Electrolytic method** : The alkali and alkaline earth metals may be obtained by the electrolysis of their fused salts.



Aluminium is obtained by the electrolysis of fused alumina dissolved in cryolite.

(v) **Precipitation method** : Certain less electropositive metals like silver, gold are precipitated when more electropositive metals are added to their complex salt solutions.



**Refining** : The metals so obtained are generally impure. They are refined by the following processes :

(i) **Distillation** : The metals having low boiling points are refined by distillation.

(ii) **Liquation** : The metals having low melting points, e.g., Sn, Pb are purified by this process.

The impure metal is melted on the sloping hearth of a reverberatory furnace when the pure metal melts down leaving behind infusible impurities.

(iii) **Oxidation** : The method is used for the refining of metals, e.g., Sn when the impurities are more readily oxidized than the metal itself.

(iv) **Electrolytic method** : Most of the metals are refined by the electrolysis of a solution of a soluble salt of metal. The impure metal is made the anode and pure metal is made the cathode. On electrolysis, pure metal is deposited at cathode, whereas the impurities either dissolve out or fall down below anode as *anode mud*. The process is used for the refining of copper, silver, chromium etc.

## • 9.2 METALLURGY OF TITANIUM

### Occurrence :

It is widely distributed in nature and is one of the ninth most abundant elements. The chief minerals are :

	% of $\text{TiO}_2$
(i) <b>Ilmenite</b> — $\text{FeTiO}_3$	60%
(ii) <b>Rutile</b> — $\text{TiO}_2$	90%
(iii) <b>Titanite</b> — $\text{CaTiSiO}_5$	34–42%

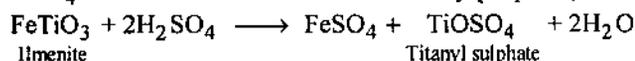
The important ores from which the metal is extracted are ilmenite and rutile. Ilmenite occurs largely in America, Russia, Australia and India. In India, it occurs largely in Kerala. Rutile occurs largely in Norway and England.

### Extraction

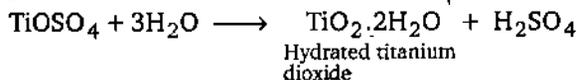
#### 1. From Ilmenite :

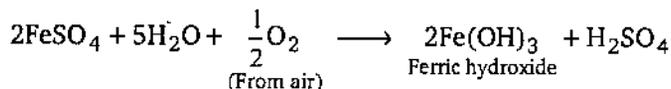
(i) **Preparation of  $\text{TiO}_2$  or  $\text{TiCl}_4$**  : These can be obtained from the following methods.

(a) **Acid process** : The concentrated ore is treated with conc.  $\text{H}_2\text{SO}_4$  when iron present in the ore is converted into  $\text{FeSO}_4$  and titanium is converted into titanyl sulphate,  $\text{TiOSO}_4$ .

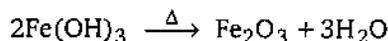
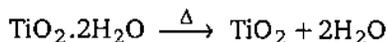


The resulting product is extracted with water and then concentrated when hydrated  $\text{TiO}_2$  and  $\text{Fe}(\text{OH})_3$  are precipitated.

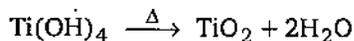
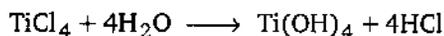
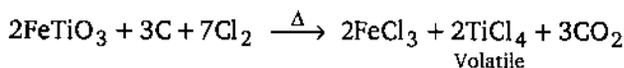




These precipitates are filtered, washed with water and then heated at high temperature when  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  are obtained.

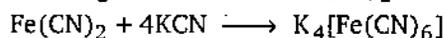
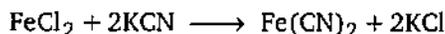


**(b) Chlorine Process :** The concentrated ore is mixed with carbon and  $\text{Cl}_2$  is passed over the heated mixture. The volatile  $\text{TiCl}_4$  is obtained which on hydrolysis and heating gives  $\text{TiO}_2$ .

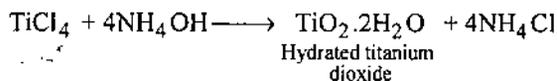


**(ii) Removal of  $\text{Fe}_2\text{O}_3$  and  $\text{FeCl}_3$  from  $\text{TiO}_2$  and  $\text{TiCl}_4$ .**

$\text{TiO}_2$  as obtained from acid process and  $\text{TiCl}_4$  as obtained from chlorine process contain the impurities of  $\text{Fe}_2\text{O}_3$  and  $\text{FeCl}_3$ , respectively. The impure titanium compound is dissolved in conc.  $\text{HCl}$  and the resulting solution is treated with  $\text{NaHSO}_3$  solution when  $\text{Fe}^{+3}$  ions are reduced to  $\text{Fe}^{+2}$ . Now the solution is boiled, when unreacted  $\text{NaHSO}_3$  is decomposed. The remaining solution is now treated with  $\text{KCN}$ , when  $\text{Fe}^{+2}$  forms complex compound  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .

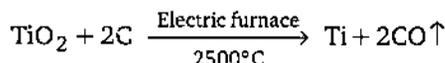


The  $\text{NH}_4\text{OH}$  solution is now added when hydrated  $\text{TiO}_2$  is precipitated leaving behind  $\text{K}_4[\text{Fe}(\text{CN})_6]$  in solution.

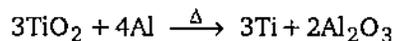


**(iii) Reduction of  $\text{TiO}_2$  or  $\text{TiCl}_4$**

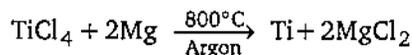
**(a) By carbon**



**(b) By aluminothermic process**



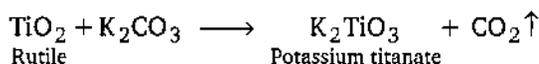
**(c) By Kroll's process.**

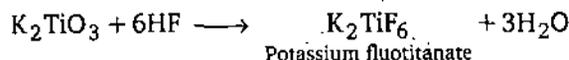


Titanium obtained by above methods is not pure.

**(2) From Rutile**

**Wohler's Process :** In this process the finely powdered rutile is fused with an excess of  $\text{K}_2\text{CO}_3$  and the resulting product is treated with dil. hydrofluoric acid. The sparingly soluble potassium fluotitanate so obtained is boiled with excess of water to dissolve all the salt. The hot solution of the salt is filtered and then cooled when the crystals of potassium fluotitanate are obtained. These crystals are now again dissolved in hot water and then treated with  $\text{NH}_4\text{OH}$  when the precipitate of hydrated  $\text{TiO}_2$  is obtained. This precipitate is filtered, washed and then heated when  $\text{TiO}_2$  is obtained.

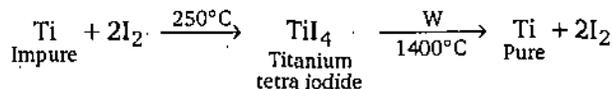




Pure titanium may be obtained from  $\text{TiO}_2$  as mentioned below.

### Purification of Titanium

**Van Arkel method :** The impure titanium obtained by above methods is heated with iodine at  $250^\circ\text{C}$  when titanium tetra iodide is obtained. The vapours of titanium tetra iodide are passed over tungsten filament heated at  $1400^\circ\text{C}$  when pure titanium is obtained.

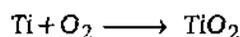


### Properties of Titanium

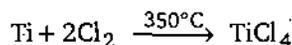
**Physical properties :** Titanium is a shining white metal having a high melting point  $1670^\circ\text{C}$  and a high boiling point  $3275^\circ\text{C}$ . It is paramagnetic.

**Chemical properties :**

(1) **Action of air :** It is stable in air upto  $120^\circ\text{C}$  but at higher temperatures it catches fire to form  $\text{TiO}_2$ .

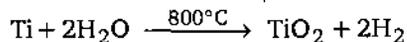


(2) **Action of halogens :** It reacts with halogens at different temperatures to form tetra halides.

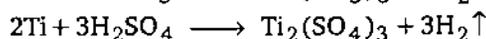
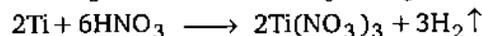
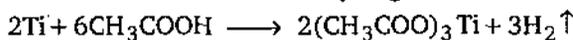


(3) **Action of non-metals :** It reacts with non-metals like boron, carbon, nitrogen and hydrogen to form interstitial compounds-borides, carbides, nitrides and hydrides, respectively.

(4) **Action of water :** It does not react with water at ordinary temperature but decomposes steam at  $800^\circ\text{C}$ .



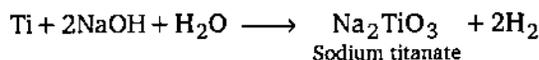
(5) **Action of acids :** It reacts with dil. acids to form hydrogen.



Hot and conc.  $\text{H}_2\text{SO}_4$  however gives  $\text{SO}_2$



6. **Action of alkalis :** It reacts with fused alkalis to form hydrogen.



### Uses of Titanium :

(i) **As alloys :** The most important alloy of titanium is ferrotitanium which is used to remove  $\text{H}_2$  and  $\text{O}_2$  in ferrous and non-ferrous metallurgies.

(ii)  $\text{TiO}_2$  is used as a pigment. It is also used in cosmetics as a whitener in face powders, cold creams, skin lotions, etc.

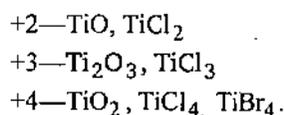
(iii)  $\text{TiCl}_4$  is used in war times for the production of irritating smoke clouds and dense fog formation.

(iv) Titanium compounds are used in dyeing paper, cotton, wool and leather.

(v)  $\text{TiCl}_3$  is used as a reducing agent in the laboratory.

## Oxidation States of Titanium

(b) The outer configuration of titanium is  $3d^2 4s^2$ . It shows oxidation states +2, +3 and +4. The oxidation state +2 arises when  $s$ -electrons are involved in the bond formation and +3 and +4 oxidation states arise when one or both the  $(n-1)$   $d$  electrons are also involved in the bond formation. The most common and stable oxidation state of titanium is +4. Some compounds in the various oxidation states of titanium are :



## • 9.3. METALLURGY OF VANADIUM

### Occurrence :

Vanadium does not occur in the free state. In the combined state it is widely distributed in nature although in very small amounts. The chief ores are :

(i) **Carnotite** :  $\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ . It contains upto 20%  $\text{V}_2\text{O}_5$ .

(ii) **Vanadinite** :  $3\text{Pb}_3(\text{VO}_4)_2 \cdot \text{PbCl}_2$ . It contains upto 8–21%  $\text{V}_2\text{O}_5$ .

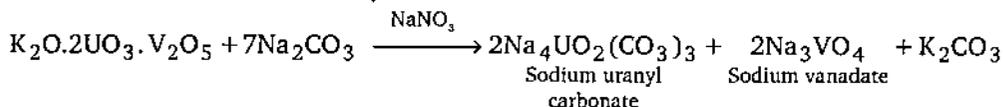
(iii) **Patronite** :  $\text{V}_2\text{S}_5 \cdot 3\text{CuS}_2$ . It contains upto 30%  $\text{V}_2\text{O}_5$ .

Small amounts of vanadium are also found in copper, iron and lead ores. Vanadium minerals are found in South Africa and Spain. The coal dust obtained from South Africa contains 40%  $\text{V}_2\text{O}_5$ .

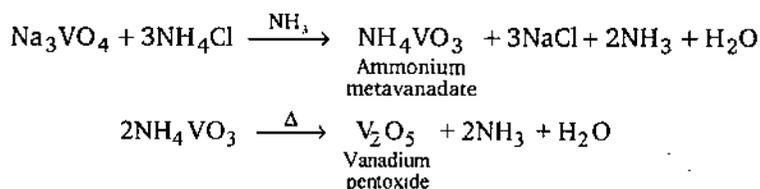
### Extraction

#### (1) From carnotite.

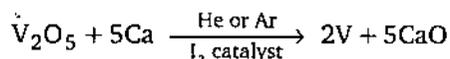
(a) **Preparation of  $\text{V}_2\text{O}_5$**  : The concentrated ore is fused with a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaNO}_3$  and the fused mass is extracted with water when iron is precipitated as  $\text{Fe}(\text{OH})_3$ . The remaining solution is now concentrated when the crystals of sodium uranyl carbonate are obtained while sodium vanadate remains in the mother liquor.



The crystals of sodium uranyl carbonate are separated and the remaining solution is treated with  $\text{NH}_4\text{Cl}$  and then saturated with  $\text{NH}_3$ . The orange precipitate of ammonium metavanadate is obtained which on heating gives  $\text{V}_2\text{O}_5$ .

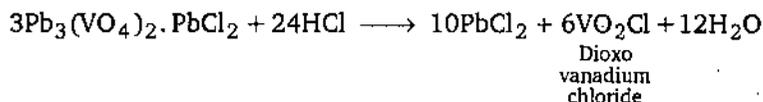


(b) **Reduction of  $\text{V}_2\text{O}_5$**  : The  $\text{V}_2\text{O}_5$  so obtained is reduced with calcium in an inert atmosphere of helium or argon in the presence of iodine as catalyst.

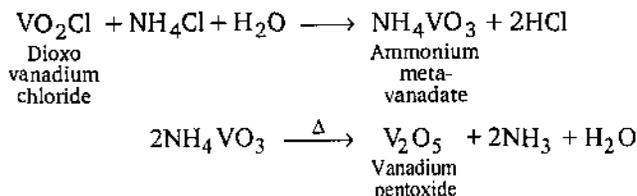


#### (2) From vanadinite.

(a) **Preparation of  $\text{V}_2\text{O}_5$**  : The concentrated ore is treated with conc.  $\text{HCl}$ . The solution is cooled when  $\text{PbCl}_2$  is precipitated and dioxo vanadium chloride remains in the solution.



The precipitate of  $\text{PbCl}_2$  is separated by filtration and the remaining solution is treated with  $\text{NH}_4\text{Cl}$  and then saturated with  $\text{NH}_3$ . The orange precipitate of ammonium metavanadate is obtained which on heating gives  $\text{V}_2\text{O}_5$ .



The  $\text{V}_2\text{O}_5$  so obtained is reduced to vanadium by the above method.

### Properties of Vanadium

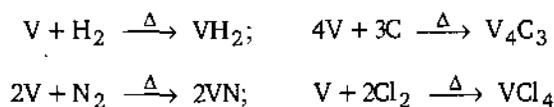
**Physical properties :** It is a silvery white metal. It is brittle, hard and is a good conductor of electricity. It has high melting point  $1915^\circ\text{C}$ .

**Chemical properties :**

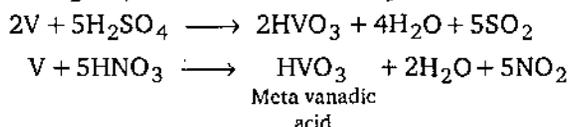
(i) **Action of air :** It is stable in air at ordinary temperature but on heating it is oxidized to give pentoxide.



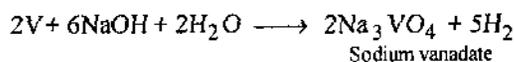
(ii) **Action of non-metals :** It reacts with non-metals at high temperature to form corresponding compounds.



(iii) **Action of acids :** It does not react with the mineral acids at ordinary temperatures. It, however, reacts with hot conc.  $\text{H}_2\text{SO}_4$  or with hot conc.  $\text{HNO}_3$  to form meta vanadic acid.



(iv) **Action of alkalis :** It reacts with fused alkalis to form hydrogen.



### Uses of Vanadium :

(i) **As alloys :** The most important alloy of vanadium is ferro vanadium which is used in the steel industry to remove oxygen and nitrogen. Vanadium steel is used in motor cars and high speed tools.

(ii)  $\text{V}_2\text{O}_5$  is used as a catalyst in the contact process for the manufacture of  $\text{H}_2\text{SO}_4$ .

(iii)  $\text{V}_2\text{O}_5$  is also used as an oxidizing agent in the organic chemistry.

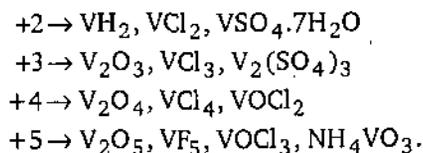
(iv) Vanadium compounds are used in the manufacture of ink, medicines and insecticides.

(v) Vanadium compounds are also used to hasten the process of drying of paints and varnishes.

(vi) Vanadium compounds are used in glass industry.

### Oxidation States of Vanadium

(b) The outer configuration of vanadium is  $3d^3 4s^2$ . It shows oxidation states +2, +3, +4 and +5. The oxidation state +2 arises when  $s$ -electrons are involved in the bond formation and +3, +4 and +5 oxidation states arise when one, two or all the  $(n-1)d$  electrons are also involved in the bond formation. The most common and stable oxidation state of vanadium is +5. Some compounds in various oxidation states of vanadium are :



## • 9.4. METALLURGY OF CHROMIUM

### Occurrence :

Chromium does not occur free in nature. In the combined state it occurs as :

- (i) **Chromite or chrome iron stone** :  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ .
- (ii) **Chrometite** :  $\text{Fe}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$ .
- (iii) **Chrome ochre** :  $\text{Cr}_2\text{O}_3$ .
- (iv) **Crocoisite** :  $\text{PbCrO}_4$ .

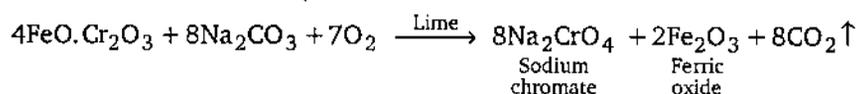
The most important ore from which the metal is extracted is chromite. It occurs in Russia, U.S.A., South Africa and India. In India it occurs in Bihar, Mysore, Madras, Orissa and Bombay.

### Extraction :

The extraction of the metal involves the following steps :

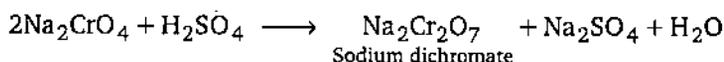
(i) **Concentration** : The ore is concentrated by gravity process, *i.e.*, it is washed with rapidly flowing current of water when lighter impurities are washed away leaving behind heavier particles of the ore.

(ii) **Roasting** : The concentrated ore is mixed with an excess of  $\text{Na}_2\text{CO}_3$  and little lime and heated on the hearth of a reverberatory furnace at  $900\text{--}1000^\circ\text{C}$  in the presence of excess of air. Lime keeps the mass porous and thus, makes the oxidation easier.



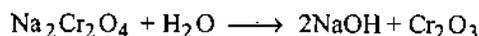
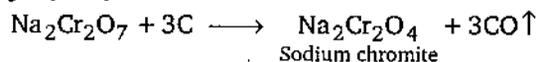
A yellow mass consisting of sodium chromate and  $\text{Fe}_2\text{O}_3$  is obtained. The product is extracted with water when sodium chromate goes in solution leaving behind  $\text{Fe}_2\text{O}_3$  and other insoluble impurities.

(iii) **Preparation of  $\text{Cr}_2\text{O}_3$**  : The yellow solution of sodium chromate is treated with dil.  $\text{H}_2\text{SO}_4$  when sodium dichromate and sodium sulphate are obtained.

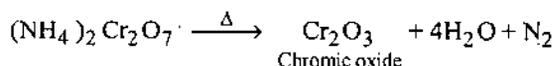
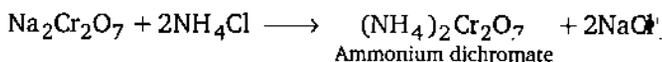


On fractional crystallization, the less soluble sodium sulphate separates out first leaving behind more soluble sodium dichromate in solution. The solution is again concentrated to get crystals of  $\text{Na}_2\text{Cr}_2\text{O}_7$ . From sodium dichromate,  $\text{Cr}_2\text{O}_3$  may be obtained by any of the following two methods

(a) The sodium dichromate is heated with carbon and sodium chromite so formed is reacted with water when  $\text{Cr}_2\text{O}_3$  is precipitated.



(b) Sodium dichromate is heated with  $\text{NH}_4\text{Cl}$  when ammonium dichromate obtained by double decomposition further decomposes to give  $\text{Cr}_2\text{O}_3$ .



(iv) **Reduction of chromic oxide** : The chromic oxide may be reduced to the metal by any of the following methods :

(a) **By carbon** :  $\text{Cr}_2\text{O}_3$  is reduced by heating with sugar charcoal in a lime crucible.



(b) **By aluminothermic process** : The  $\text{Cr}_2\text{O}_3$  is mixed with equal amount of aluminium powder. The mixture is called as thermite. It is now kept in a cavity made in a packing of fluorspar or sand in a tin. A small starter containing 15 parts  $\text{BaO}_2$  and 2 parts Mg powder is immersed under the thermite.

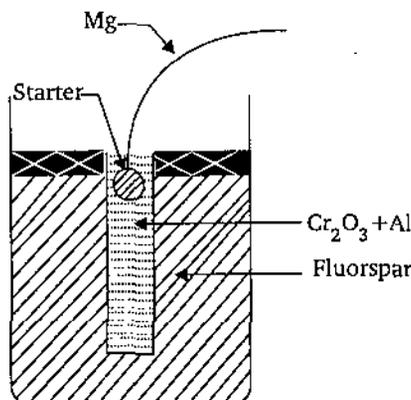
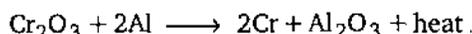
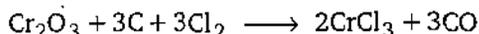


Fig. 5. Reduction of  $\text{Cr}_2\text{O}_3$  by aluminothermic process.

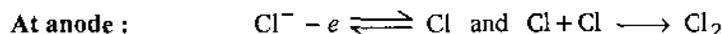
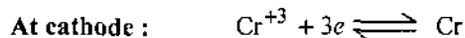
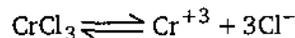
The starter is connected with a Mg wire. The Mg wire is ignited at the outer end. Soon the flame reaches the starter and the whole mass bursts into flame. The metal oxide is reduced to the metal. The metal is obtained in the molten state due to the large amount of heat produced during the reaction. Fluorspar or sand saves the loss of heat by radiation.



(c) **Electrolytic method** : The chromic oxide so obtained is mixed with carbon and then  $\text{Cl}_2$  is passed over the heated mixture.



Chromic chloride is extracted with water and then electrolysed using carbon anode and mercury cathode. The chromium amalgam is distilled in vacuum when Hg distills over first leaving behind chromium.



### Properties of Chromium :

**Physical** : It is a silvery white hard metal. It is malleable, ductile and has a high melting point  $1840^\circ\text{C}$  and boiling point  $2200^\circ\text{C}$ . It is paramagnetic.

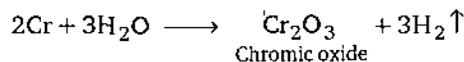
**Chemical** : (i) *Action of air* : The metal is stable in air but when heated to a high temperature in oxy hydrogen flame, it is oxidized to chromic oxide.



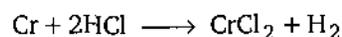
(ii) *Action of halogens* : The metal reacts directly with halogens to form chromic halides.



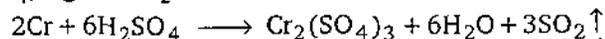
(iii) *Action of water* : It is not affected by water but decomposes steam at high temperature to give  $\text{H}_2$ .



(iv) *Action of acids* : It reacts with dil. HCl or dil.  $\text{H}_2\text{SO}_4$  to give  $\text{H}_2$ .



On heating with conc.  $\text{H}_2\text{SO}_4$ , it gives  $\text{SO}_2$ .



The metal does not react with dil.  $\text{HNO}_3$  whereas it becomes passive by conc.  $\text{HNO}_3$ .

### Use of Chromium :

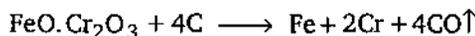
- (1) Chromium is used mostly in the production of various kinds of steels.
- (2) On account of its high polish and anti-corrosive nature, it is used in chrome plating.

(3) Chromium compounds are used in dyeing, in tanning of leather, in the preparation of coloured pigments for paint industry and as oxidizing agents.

(4) The chromite ore is used as a refractory material for inner lining of furnaces.

### Alloys of Chromium and its Uses :

(i) **Ferrochrome** : It is an alloy of iron and chromium containing about 70% of chromium. It is prepared by reducing chromite ore with carbon in a Moissan's electric furnace.



It is used for alloying with iron to make special steels.

(ii) **Stainless steel** : This alloy containing 12% chromium and 0.1 to 0.4% carbon is used for household wares and cutlery.

(iii) **Chromium vanadium steel** : This alloy is very hard and strong and is used for gears and locomotive wheels.

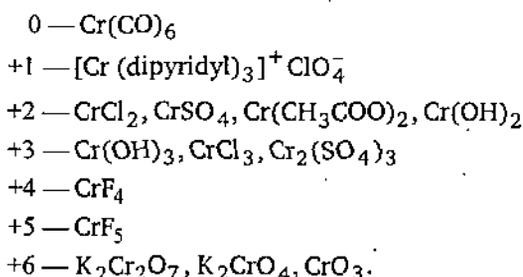
(iv) **Chromium tungsten steel** : This alloy is used for high speed tools.

(v) **Nichrome** : It is an alloy of chromium, nickel and iron. This alloy is resistant to atmospheric corrosion and can withstand high temperature. It is very much used in electrical resistances.

(vi) **Stellite** : It is an alloy of chromium, cobalt and tungsten and is used for making surgical instruments and high speed tools.

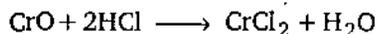
### Oxidation States of Chromium and Compounds :

The outer electronic configuration of chromium is  $3d^5 4s^1$ . It shows oxidation states ranging from 0 to +6. The oxidation state zero arises in the metal carbonyls. The oxidation state +1 is shown in certain complexes when  $ns^1$  electron is involved in the bond formation. The oxidation states +2 to +6 arise when  $d$ -electrons are also successively involved in the bond formation. The most important and stable oxidation states of chromium are +2, +3 and +6. Some compounds in the various oxidation states of chromium are :

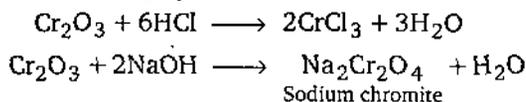


Chromium forms three important oxides, *i.e.*,  $\text{CrO}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{CrO}_3$  in +2, +3 and +6 oxidation states. The acidic character of these oxides increase with the increase in the oxidation state of the metal. This is justified because of the following facts :

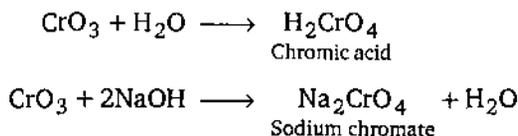
(i) Chromous oxide ( $\text{CrO}$ ) is basic as it reacts with acids to form salts



(ii) Chromic oxide ( $\text{Cr}_2\text{O}_3$ ) is amphoteric as it reacts with both acids and alkalis to form salts.



(iii) Chromic anhydride ( $\text{CrO}_3$ ) is acidic as it reacts with water to form acid and reacts with alkalis to form salts.



## • 9.5. METALLURGY OF NICKEL

### Occurrence :

It does not occur free in nature. In the combined state, it is generally found associated with S, As, Fe, Co and Cu. The chief minerals are:

- (i) Pentlandite—(Ni, Cu, Fe) S : It contains about 22% nickel.
- (ii) Kupfer nickel or niccolite—NiAs
- (iii) Nickel glance—NiAsS
- (iv) Nickel blende—NiS
- (v) Garnierite :  $\text{NiMgSiO}_3 \cdot x\text{H}_2\text{O}$ . It contains about 8% nickel.

The chief ore from which the metal is extracted is pentlandite. It occurs in the Sudbury mines of Ontario in Canada. About 90% of nickel comes from this ore. Nickel ores are also found in Russia, America, Australia, Spain and Norway. In India, small amount of nickel associated with copper ores is found in Rajasthan and with iron ores is found in Bihar.

### Extraction :

The extraction of the metal from pentlandite involves the following steps :

(i) **Concentration** : The ore is concentrated by froth floatation method. The finely powdered ore is mixed with water and oil and air is passed through the mixture. The ore particles are easily wetted by the oil and come to the surface whereas impurities are settled down.

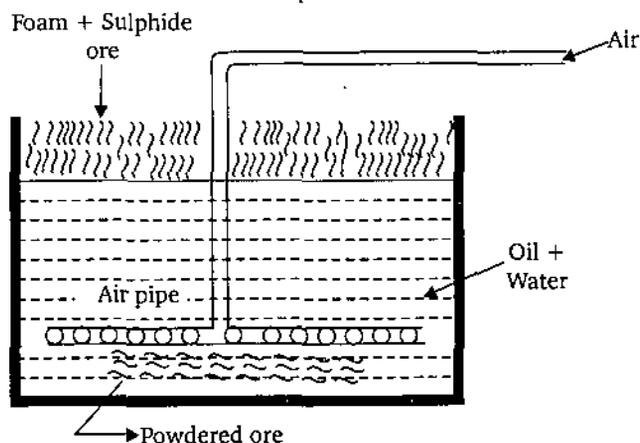
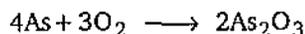
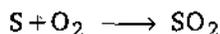


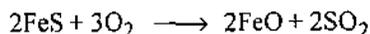
Fig. 6. Concentration of pentlandite by froth floatation process

(ii) **Roasting** : The concentrated ore is heated in the presence of excess of air when the following reactions take place.

- (a) Sulphur and arsenic are volatilized off as their oxides.

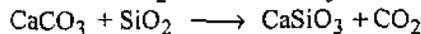
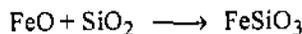


- (b) Ferrous sulphide is partly converted into ferrous oxide.



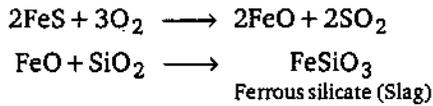
The sulphides of copper and nickel remain unaffected.

(iii) **Smelting** : The resulting product is mixed with silica, coke and lime stone and smelted in a blast furnace when most of the ferrous sulphide left during roasting is converted into ferrous oxide. Some ferric oxide formed during these oxidation reactions is reduced by coke to form ferrous oxide. Ferrous oxide, thus, obtained during roasting and smelting reacts with silica to form ferrous silicate. Lime stone also reacts with silica to form calcium silicate.



The mixture of ferrous and calcium silicates float over nickel and copper sulphides and is removed as slag. The product still contains some iron and is called as crude matte.

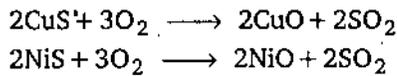
(iv) **Bessemerization** : The crude matte still contains some iron sulphide which is removed by Bessemer converter. The crude matte is mixed with sufficient quantity of silica and heated in a Bessemer converter. The air is passed at high pressure over the heated mixture when remaining iron sulphide is converted into iron oxide which combines with silica to form iron silicate. This iron silicate is removed as slag.



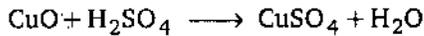
The resulting product is known as refined matte. It contains 55% nickel, 25–30% copper, 15–16% sulphur and 0.2–0.4% iron.

(v) **Conversion of refined matte into nickel** : The nickel is obtained from refined matte by the following steps –

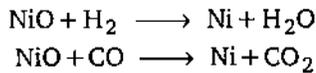
(a) The refined matte is roasted in a special furnace when copper and nickel sulphides are converted into their oxides.



(b) The resulting mixture of oxides is treated with dil.  $\text{H}_2\text{SO}_4$  when most of the copper oxide dissolves to form  $\text{CuSO}_4$  whereas  $\text{NiO}$  remains, unaffected by dil.  $\text{H}_2\text{SO}_4$ .



(c) The nickel oxide is reduced by water gas at 300–350°C when nickel is obtained.



(vi) **Purification** : The nickel so obtained contains the impurities of copper, iron and cobalt etc. This is purified by Mond's process and electrolytic process.

(a) **Mond's process** : This process is based upon the fact that nickel reacts with carbon monoxide at 50–60°C to form volatile nickel carbonyl which is decomposed at 180–200°C to form nickel and carbon monoxide. This CO can be used again for the purification of nickel.

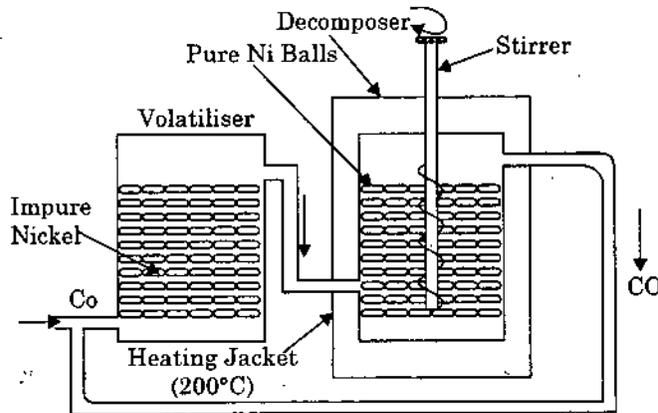
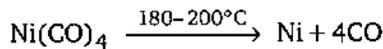
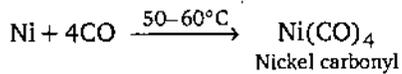


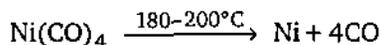
Fig. 7. Purification of nickel by Mond's process.



The apparatus contains two parts.

(i) **Volatilizer** : It contains impure nickel. Carbon monoxide is passed at 50–60°C when volatile nickel carbonyl is obtained whereas impurities remain unaffected.

(ii) **Decomposer** : It contains pure nickel shots which are kept in motion by means of mechanical stirrer. These shots are heated by heating jacket at 180–200°C. The vapours of nickel carbonyl coming from volatilizer are decomposed at this temperature to form nickel and carbon monoxide.



Nickel so obtained is deposited on pure nickel shots and carbon monoxide is again taken to volatilizer. The whole process is done carefully because both CO and Ni(CO)<sub>4</sub> are very poisonous.

(b) **Electrolytic method** : The purification of nickel is done by electrolytic method. In this method, the saturated solution of nickel ammonium sulphate is electrolysed using impure nickel as anode and pure nickel as cathode. Nickel is deposited on the cathode.

### Properties of Nicol :

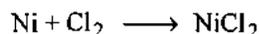
**Physical properties** : Nicol is a soft silvery white metal, quite malleable and ductile. It has a high melting point 1453°C and boiling point 2900°C. It is ferromagnetic, *i.e.*, strongly paramagnetic. It has high thermal and electrical conductivities. The finely divided metal absorbs 17 times its volume of hydrogen.

#### Chemical properties :

(i) **Action of air** : The metal is stable in air at ordinary temperatures but burns in oxygen to form nickelous oxide.



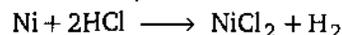
(ii) **Action of halogens** : The metal reacts directly with dry halogens to form halides.



(iii) **Action of water** : It is not affected by water but decomposes steam at high temperature to give H<sub>2</sub>.



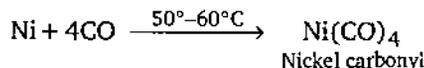
(iv) **Action of acids** : It slowly reacts with dil. HCl or dil. H<sub>2</sub>SO<sub>4</sub> to give H<sub>2</sub>.



The metal dissolves readily in dil. HNO<sub>3</sub> but becomes passive by conc. HNO<sub>3</sub>. This is due to the formation of oxide layer on the metal surface.



(v) **Action with carbon mono oxide** : The metal reacts with CO at about 50°–60°C to form volatile nickel carbonyl which is used in the purification of nickel by Mond's process.



### Uses of Nickel :

(i) The main use of nickel is in the form of its alloys. Some of its alloys and uses are as follows :

(a) **German silver** : It contains Cu = 60%, Ni = 20% and Zn = 20%. It is used in making cheap ornaments and utensils.

(b) **Monel metal** : It contains Ni = 60% and Cu = 40%. It is used in chemical industries and in turbine blades.

(c) **Cupro nickel** : It contains Ni = 25% and Cu = 75%. It is used in making coins.

(d) **Invar** : It contains Ni = 35%, C = 0.3% and rest iron. It is used in making clock pendulums.

(e) **Nichrome** : It contains Ni = 60%, Fe = 25% and Cr = 15%. It is used in making electrical resistance wires.

(f) **Nickel steel** : It contains Ni = 35% and rest iron. It is used in making high speed tools, heavy guns and underground wires.

(ii) The most important use of nickel is in nickel plating.

(iii) It is used as catalyst in the manufacture of vegetable ghee.

(iv) The electrodes and crucibles of nickel are used in the laboratory and in the industry.

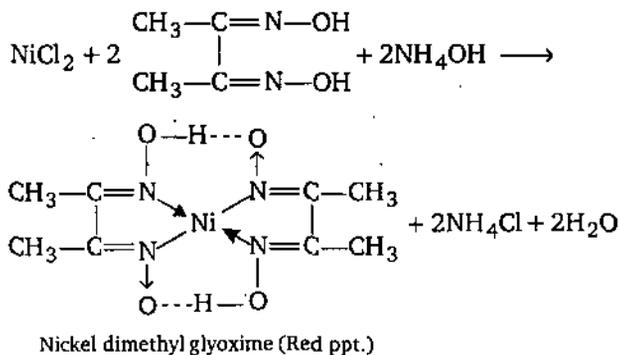
### Oxidation States of Nickel :

The outer electronic configuration of nickel is 3d<sup>8</sup> 4s<sup>2</sup>. It shows oxidation states 0, +2, +3 and +4. The zero oxidation state is found in Ni(CO)<sub>4</sub>. The +2 oxidation state is its most stable oxidation state.

and arises when *s*-electrons are involved in the bond formation. The oxidation states +3 and +4 arise when one or two *d*-electrons are also involved in the bond formation. Some of the compounds in these oxidation states are as follows :



**Test of nickel when it is present in traces in a sample.** The given sample is dissolved in dil. HCl and then solution is made alkaline with  $\text{NH}_4\text{OH}$ . Now alcoholic solution of dimethyl glyoxime is added to the above solution. Formation of red precipitate of nickel dimethyl glyoxime complex indicates the presence of nickel.



## • 9.6. METALLURGY OF PLATINUM

### Occurrence :

Platinum occurs in nature as fine particles mixed with sand and gravel. It is also found associated with the metals of its own group in the form of alloys and with other metals like copper and gold. In the combined state it occurs in small amounts in the form of following minerals :

- (i) **Braggite** : (Pt, Pd, Ni) S
- (ii) **Sperrylite** :  $\text{PtAs}_2$
- (iii) **Cooperite** : PtS

Ural mountains are the chief sources of platinum and Russia contributes about 90% of the total world supply of platinum. Now a days, platinum is also obtained from the residue of Mond's process of purification of nickel.

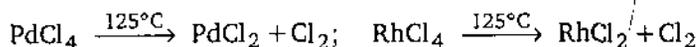
### Extraction :

#### (1) From Native Alloy :

(a) **Concentration** : The platinum bearing sand, gravel or rocks are finely powdered and washed with rapidly flowing current of water when lighter impurities are washed away leaving behind heavier metallic particles. The concentrated alloy contains gold, palladium, rhodium and iridium associated with platinum which are removed as follows :

(b) **Removal of gold** : The concentrated alloy is shaken with mercury when gold forms an amalgam and is removed.

(c) **Removal of palladium and rhodium** : The residue so obtained is now dissolved in aqua regia when tetrachlorides of platinum metals are obtained. This solution is filtered to remove any insoluble impurities and evaporated to dryness. The residue is heated at  $125^\circ\text{C}$  when tetrachlorides of palladium and rhodium form insoluble dichlorides whereas tetrachlorides of platinum and iridium remain unaffected.



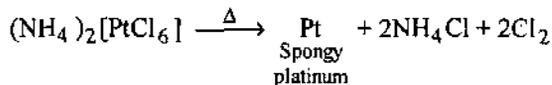
The residue is extracted with water to obtain soluble  $\text{PtCl}_4$  and  $\text{IrCl}_4$ .

(d) **Removal of iridium** : The solution of  $\text{PtCl}_4$  and  $\text{IrCl}_4$  is acidified with HCl and treated with saturated solution of  $\text{NH}_4\text{Cl}$  when a precipitate of ammonium hexachloro platinate is obtained leaving behind other metals in solution.





(e) **Preparation of platinum metal** : The precipitate of ammonium hexachloro platinate is washed, dried and ignited when spongy platinum is obtained.



The spongy platinum is heated at 3400°C in the presence of oxygen in lime crucible when silvery white platinum is obtained.

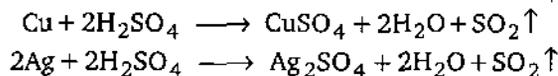
## (2) From the Residue of Mond's Process

After the purification of nickel by Mond's process, the residue in addition to 1.8% Pt, also contains silver, copper and other platinum metals. Now a days, this is the main source for the extraction of platinum. The extraction of platinum from it involves the following steps :

(a) **Concentration** : The residue is mixed with PbO, coke and sodium carbonate and heated in a reverberatory furnace when impurities are removed as slag. Coke reacts with lead oxide to form lead which forms alloy with these metals. This alloy is now subjected to cupellation, *i.e.*, heated in the bone ash crucibles when lead is oxidized to PbO and is then removed.

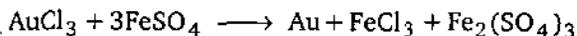
(b) **Removal of impurities** : The concentrated product so obtained contains the impurities of Ag, Cu, Au, Pd, Rh and Ru which are removed as follows :

(i) **Removal of copper and silver** : The concentrated product is boiled with conc.  $\text{H}_2\text{SO}_4$  when silver and copper in the form of their sulphates and a part of palladium as  $\text{PdSO}_4$  go into the solution.

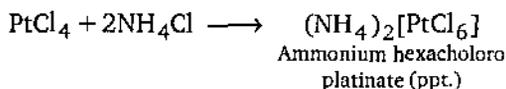


(ii) **Removal of rhodium and ruthenium** : The remaining product is now treated with aqua regia when gold, platinum and palladium form soluble chlorides, whereas rhodium and ruthenium remain insoluble.

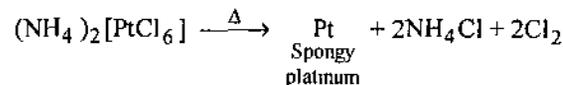
(iii) **Removal of gold** : The solution of chlorides is treated with freshly prepared solution of  $\text{FeSO}_4$  when gold is precipitated.



(iv) **Removal of palladium** : The remaining solution is acidified with HCl and treated with saturated solution of  $\text{NH}_4\text{Cl}$  when a precipitate of ammonium hexachloro platinate is obtained leaving behind other metals in the form of their soluble salts in solution.



(v) **Preparation of Platinum** : The precipitate of ammonium hexachloro platinate is washed, dried and ignited when spongy platinum is obtained.



The spongy platinum is heated at 3400°C in the presence of oxygen in a lime crucible when silvery-white platinum is obtained.

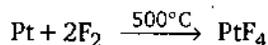
## Properties of Platinum :

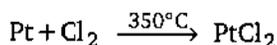
**Physical properties** : Platinum is silvery white metal. It is malleable, ductile and has a high melting point 1769°C and boiling point 4100°C. The finely divided metal absorbs 900 times its volume of hydrogen.

### Chemical properties :

(i) **Action of air** : It is a noble metal and is not affected by heating in air or oxygen. The fused metal absorbs oxygen which is given out on cooling. The phenomenon is known as spitting.

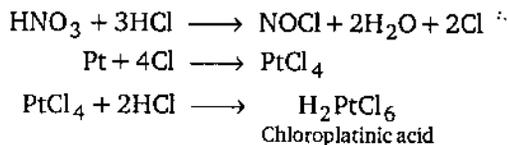
(ii) **Action of halogens** : The metal reacts directly on heating with halogens to form halides.





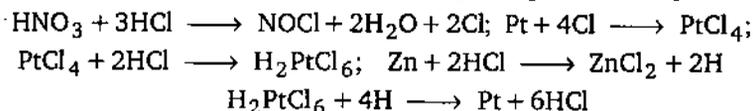
(iii) **Action of water** : It is not affected by water or by steam even at high temperatures.

(iv) **Action of acids** : It is resistant to the action of acids. It, however, reacts with aqua regia to give chloro platinumic acid.



### Different Forms of Platinum :

(i) **Platinum black** : Platinum is dissolved in aqua regia, when chloro platinumic acid is obtained. This solution is reduced by zinc and acid, formaldehyde or glucose when platinum black is obtained.



(ii) **Colloidal platinum** :

(a) **Bredig's arc method** : The method is used for the preparation of colloidal solution of platinum. In this method, two platinum electrodes are dipped in water (dispersion medium) containing some KOH, the water is cooled by freezing mixture. The electricity is passed through the metal electrodes. The intense heat of the arc turns the metal into vapours which are then condensed to form the particles of colloidal size. KOH stabilizes the colloidal solution formed.

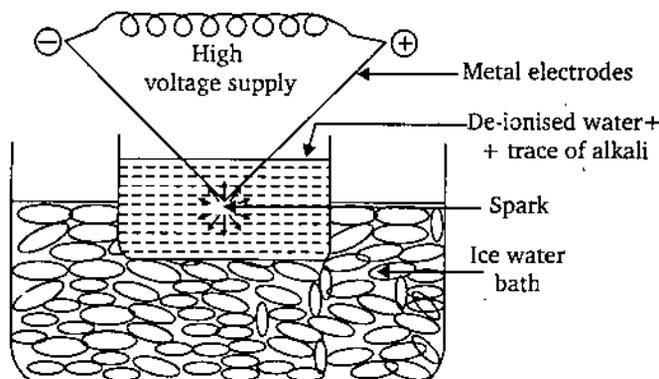
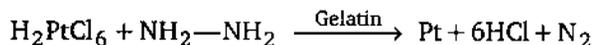


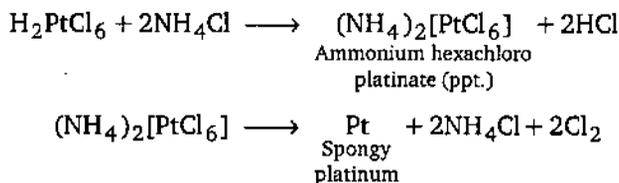
Fig. 8. Preparation of colloidal platinum

(b) Platinum is dissolved in aqua regia when chloro platinumic acid is obtained. This is now reduced by hydrazine in the presence of gelatin when colloidal platinum is obtained.



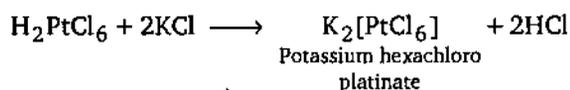
(iii) **Platinized asbestos** : Platinum is dissolved in aqua regia when chloro platinumic acid is obtained. Now asbestos fibres are separately boiled with conc. HCl and then dipped into the solution of chloro platinumic acid. The asbestos fibres are heated at 500°C. Chloro platinumic acid is decomposed to give platinum which sets on asbestos fibres. This is known as platinized asbestos.

(iv) **Spongy platinum** : Platinum is dissolved in aqua regia when chloro platinumic acid is obtained. Now this is treated with saturated solution of  $\text{NH}_4\text{Cl}$  when a precipitate of ammonium hexachloro platinate is obtained. This precipitate is filtered, washed, dried and then ignited when spongy platinum is obtained.

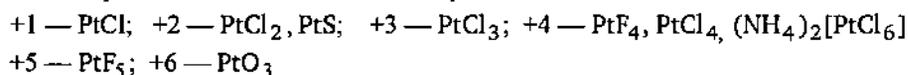


**(v) Potassium hexachloro platinate :**

Chloro platinum acid obtained from platinum as above, is treated with KCl solution when potassium hexachloro platinate is obtained.

**Oxidation States of Platinum and Compounds :**

The outer configuration of platinum is  $5d^9 6s^1$ . This shows oxidation states +1, +2, +3, +4, +5 and +6. The +1 oxidation state arises when *s*-electrons are involved in the bond formation. The other oxidation states arise when *d*-electrons are also involved in the bond formation. The most important oxidation state of platinum is +4. Some of the compounds in these oxidation states are as follows :

**• SUMMARY**

- The compounds of metals which occur in nature along with earthy impurities are known as **minerals**.
- The minerals from which the metals can be obtained economically and conveniently are known as **ores**.
- Sulphide ores of metals are generally concentrated by froth floatation process.
- **Roasting** is the process in which the ore is heated strongly in the presence of air in a reverberatory furnace. During roasting the volatile impurities are removed and the ore is partially or completely changed into oxide.
- **Calcination** is the process in which the ore is heated strongly in the absence of air to remove moisture, carbon dioxide and other volatile impurities.
- **Smelting** is the process in which finely powdered ore is heated with coke and flux at a high temperature so as to obtain the metal in the fused state.
- The oxides of metals which remain unaffected by carbon are reduced by aluminium. This process is called **aluminothermic process**.
- The important ores of titanium are ilmenite (FeTiO<sub>3</sub>) and rutile (TiO<sub>2</sub>).
- The main oxidation states of titanium are +2, +3 and +4.
- The chief ores of vanadium are carnotite (K<sub>2</sub>O·2U<sub>3</sub>O<sub>8</sub>·V<sub>2</sub>O<sub>5</sub>·3H<sub>2</sub>O) and vanadinite [(3Pb<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub>·PbCl<sub>2</sub>)].
- The main oxidation states of vanadium are +2, +3, +4 and +5.
- Vanadium is used in making alloys.
- The main ore of chromium is chromite FeO·Cr<sub>2</sub>O<sub>3</sub>.
- Chromium compounds are used in dyeing tanning of leather etc.
- The chromite ore is used as a refractory material for inner lining of furnaces.
- Chromium makes a number of alloys with metals, e.g., ferrochrome, stainless steel, nichrome etc. which are quite useful in different fields.
- The oxidation states of chromium are from zero to +6.
- The main ore of nickel is pentlandite (Ni, Cu, Fe) S.
- Mond's process is used to purify nickel.
- Nickel makes a number of alloys like german silver, monel metal, invar, nichrome, nickel steel etc.
- Nickel is used as a catalyst in the manufacture of vegetable ghee.
- The oxidation states of nickel are zero, +2, +3 and +4.
- Nickel can be tested by dimethylglyoxime tests. This consists in treating the nickel salt with dil. HCl. The solution is made alkaline. Then a few drops of alcoholic solution of dimethylglyoxime is added to the above resulting solution. Formation of a cherry red precipitate confirms the presence of nickel.
- The ore of platinum is braggite [Pt, Pd, Ni] S].

- Platinum is generally extracted from native alloy.
- Platinum can be converted into different forms like platinum black, colloidal platinum, platinised asbestos (used as a catalyst), spongy platinum etc.
- The oxidation states of platinum are +1 to +6.

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• **STUDENT ACTIVITY**

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1. Write a short note on froth floatation process.

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2. Explain the terms roasting and calcination.

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3. How is titanium obtained from rutile ?

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4. Mention the alloys of chromium and their uses.

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5. What is Mond's process for the extraction of nickel ?

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6. Mention four ores of platinum.

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7. Describe the oxidation states of vanadium.

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### • TEST YOURSELF

- Describe the general methods used for the extraction of metals.
- Mention the different method used for the purification of metals.
- Explain the terms mineral and an ore.
- Write a short note on froth floatation process.
- Explain electromagnetic method for concentrating the ores of metals.
- Explain the difference between roasting and calcination.
- Define the following terms :
 

(i) Roasting	(ii) Smelting	(iii) Calcination
(iv) Aluminothermic process	(v) Liqutation	
- Give the important minerals of titanium.
- How will you extract titanium from its ore.
- Describe the important properties and uses of titanium.
- Describe the important oxidation states of titanium with examples.
- Describe the important ores of vanadium. How the metal is extracted from them.
- Describe the properties and uses of vanadium.
- What are the oxidation states of vanadium. Give atleast one compound in each oxidation state.
- How will you extract chromium from its ores ?
- Describe the properties and uses of chromium.
- Name some important alloys of chromium and state their uses.
- What are the oxidation states of chromium and mention at least one compound in each oxidation state.
- Describe the method for the extraction of nickel from its ore.
- Describe the properties and uses of nickel.
- What are the oxidation states of nickel. Mention at least one compound in each oxidation state.
- Describe dimethylglyoxime test.
- What are the main sources of platinum ? How is the metal extracted ?
- Describe important properties and uses of platinum in the inorganic synthesis.
- What are the oxidation states of platinum. Mention at least one compound in each oxidation state.
- Starting from platinum, how will you prepare the following ?
 

(i) Platinum black	(ii) Colloidal platinum
(iii) Platinized asbestos	(iv) Spongy platinum
(v) Potassium hexachloroplatinate	

**Multiple Choice Questions**

27. Aluminothermic process is :  
 (a) Oxidation (b) Reduction (c) Redox (d) None of the above
28. Froth floatation process is used for the concentration of :  
 (a) Oxide ores (b) Sulphide ores (c) Sulphate ores (d) Carbonate ores
29. The impurities present in the mineral ore called :  
 (a) Gangue (b) Alloy (c) Flux (d) Slag
30. Cinnabar is an ore of :  
 (a) Fe (b) Hg (c) Zn (d) Ni
31. Which method of purification is represented by the following equations ?  

$$\text{Ti} + 2\text{I}_2 \longrightarrow \text{TiI}_4 \xrightarrow{1400^\circ\text{C}} \text{Ti} + 2\text{I}_2$$
 (a) Mond (b) Cupellation (c) Zone refining (d) Van Arkel
32. The outer configuration of chromium (Z = 24) is :  
 (a)  $3d^4 4s^2$  (b)  $3d^5 4s^1$  (c)  $4s^2 4p^4$  (d)  $3s^2 3p^6 3d^6$
33. Which of the following oxides of chromium is amphoteric ?  
 (a) CrO (b) CrO<sub>3</sub> (c) Cr<sub>2</sub>O<sub>3</sub> (d) CrO<sub>5</sub>
34. Dimethyl glyoxime is used for the gravimetric estimation of :  
 (a) Fe<sup>2+</sup> (b) Cr<sup>3+</sup> (c) Ni<sup>2+</sup> (d) Pt<sup>2+</sup>
35. The catalyst used in the hydrogenation of oils is :  
 (a) Fe (b) Mn (c) Ni (d) Pt
36. Ore of the following metals form a volatile carbonyl compound and the property is used for the extraction of that metal. The metal is :  
 (a) Ti (b) Ni (c) Pt (d) Cr
37. Fill in the blanks :  
 (i) Rutile is an ore of .....  
 (ii) The important ore from which chromium is extracted is .....  
 (iii) Spongy platinum is obtained by heating .....  
 (iv) Mond's process is used for the purification of .....

**ANSWERS**

27. (c), 28. (b), 29. (a), 30. (b), 31. (d), 32. (b), 33. (c), 34. (c) 35. (c) 36. (b)  
 37. (i) titanium, (ii) chromite (iii) (NH<sub>4</sub>)<sub>2</sub> [PtCl<sub>4</sub>] (iv) nickel.

## 10

## STUDY OF INORGANIC COMPOUNDS

## STRUCTURE

- Titanium Dioxide
- Titanium Tetrachloride
- Chromyl Chloride
- Potassium Dichromate
- Potassium Permanganate
- Potassium Ferrocyanide
- Potassium Ferricyanide
- Chloroplatinic Acid
- Sodium Cobaltinitrite
- Sodium Nitroprusside
  - Summary
  - Student Activity
  - Test Yourself

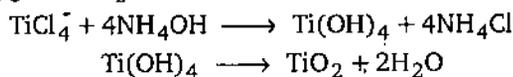
## LEARNING OBJECTIVES

After going through this unit you will learn :

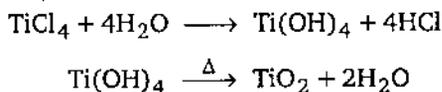
- Inorganic compounds with their properties and uses.

### • 10.1. TITANIUM DIOXIDE, $\text{TiO}_2$ (Titanic Oxide or Titania)

**Preparation :** (i) By adding ammonia solution to a solution of  $\text{TiCl}_4$ , a precipitate of  $\text{Ti}(\text{OH})_4$  is obtained which on heating gives  $\text{TiO}_2$



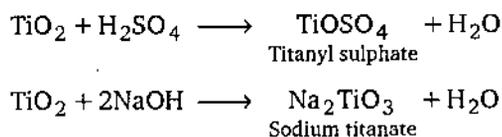
(ii) By the hydrolysis of  $\text{TiCl}_4$  with steam



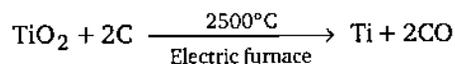
**Properties :** Titanium dioxide is a white amorphous powder, insoluble in water.

(i) **Amphoteric nature :**  $\text{TiO}_2$  is an amphoteric oxide which is more acidic than basic in character.

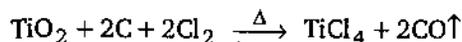
It reacts with conc. acids and fused alkalis to form salts.



(ii) **Action with carbon :**  $\text{TiO}_2$  is reduced by carbon at high temperature to form metal.



(iii) **Action with carbon and chlorine :** When  $\text{Cl}_2$  gas is passed over the heated mixture of  $\text{TiO}_2$  and carbon,  $\text{TiCl}_4$  is formed.



Uses : (i)  $\text{TiO}_2$  is used as a white pigment. It is now used in place of white lead because it is inert, non-poisonous and has a high covering power.

(ii)  $\text{TiO}_2$  is also used in cosmetics as a whitener in face powders, cold creams, skin lotions etc.

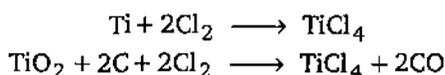
(iii)  $\text{TiO}_2$  is used in porcelain tiles and artificial teeth.

(iv)  $\text{TiO}_2$  is used in glass industry.

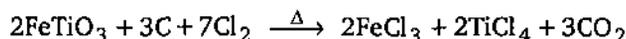
## • 10.2. TITANIUM TETRACHLORIDE, $\text{TiCl}_4$

### Preparation :

(i) By passing dry  $\text{Cl}_2$  gas over heated titanium or heated mixture of  $\text{TiO}_2$  and carbon, titanium tetrachloride is formed.

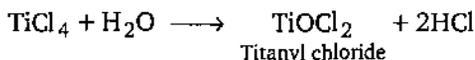


(ii) *From ilmenite* : The concentrated ore is mixed with carbon and  $\text{Cl}_2$  gas is passed over the heated mixture when volatile  $\text{TiCl}_4$  is obtained.



Properties :  $\text{TiCl}_4$  is a colourless fuming liquid, boiling point  $137^\circ\text{C}$ . It gives dense white fumes in air.

(i) *Hydrolysis* :  $\text{TiCl}_4$  is hydrolysed according to the following equations :



(ii) *Action with  $\text{NH}_3$*  :  $\text{TiCl}_4$  absorbs dry  $\text{NH}_3$  to form compounds  $\text{TiCl}_4 \cdot x\text{NH}_3$  where  $x = 4, 6, 8$

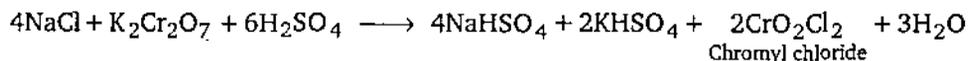
(iii)  $\text{TiCl}_4$  acts as a strong Lewis acid and forms addition compounds with alcohols or ethers of the type  $(\text{R}_2\text{O})\text{TiCl}_4$ ,  $(\text{R}_2\text{O})_2\text{TiCl}_4$  etc.

Uses :  $\text{TiCl}_4$  gives dense white fumes in air, it is, therefore, used in war times for the production of irritating smoke clouds.

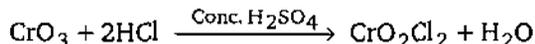
## • 10.3. CHROMYL CHLORIDE $\text{CrO}_2\text{Cl}_2$

### Preparation :

(i) Chromyl chloride is obtained by distilling a mixture of sodium chloride, potassium dichromate with conc.  $\text{H}_2\text{SO}_4$  and condensing the vapours,

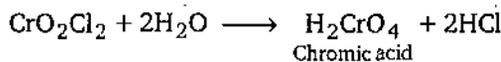


(ii) Chromyl chloride is obtained by adding small quantities of conc.  $\text{H}_2\text{SO}_4$  to a cold solution of chromic anhydride in conc.  $\text{HCl}$ .

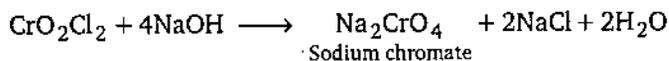


Properties :  $\text{CrO}_2\text{Cl}_2$  is a deep red liquid, boiling point  $116.7^\circ\text{C}$  and melting point  $-96.5^\circ\text{C}$ . It is soluble in the organic solvents such as  $\text{CCl}_4$ ,  $\text{CS}_2$  etc.

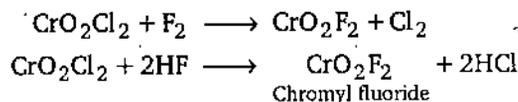
(i) *Hydrolysis* :  $\text{CrO}_2\text{Cl}_2$  is hydrolysed by water to give chromic and hydrochloric acid.



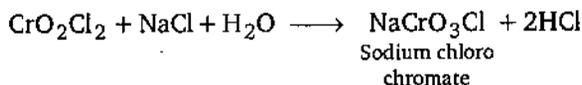
(ii) *Action with  $\text{NaOH}$*  :  $\text{CrO}_2\text{Cl}_2$  reacts with  $\text{NaOH}$  to form a yellow solution of sodium chromate.



(iii) **Action with F<sub>2</sub> or HF** : Chromyl fluoride is obtained.

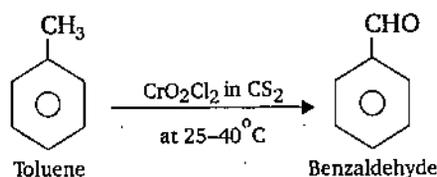


(iv) **Action with NaCl** : When CrO<sub>2</sub>Cl<sub>2</sub> vapours are passed into saturated solution of NaCl, red crystals of sodium chlorochromate are obtained.



(v) **Oxidizing properties** : CrO<sub>2</sub>Cl<sub>2</sub> is a powerful oxidizing agent and explodes in contact with burning sulphur, phosphorus, ammonia. A solution of CrO<sub>2</sub>Cl<sub>2</sub> in CS<sub>2</sub> at 25–40°C oxidizes toluene to benzaldehyde. (Etard reaction)

**Uses** : (i) CrO<sub>2</sub>Cl<sub>2</sub> is used as an intermediate product in the detection of chlorides by chromyl chloride test.

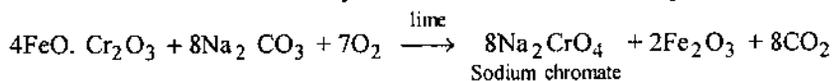


(ii) CrO<sub>2</sub>Cl<sub>2</sub> is used as an oxidizing agent in organic chemistry.

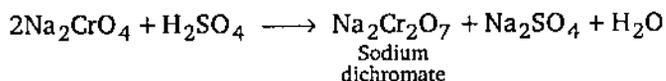
#### • 10.4. POTASSIUM DICHROMATE, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

##### Preparation :

**From chrome iron stone** : Potassium dichromate is obtained from chrome iron stone, the important ore of chromium. The concentrated ore is mixed with an excess of Na<sub>2</sub>CO<sub>3</sub> and little lime and heated on the hearth of a reverberatory furnace at 900–1000°C in the presence of excess of air.



The product is extracted with water when sodium chromate goes in solution. The yellow solution of sodium chromate is treated with dil. H<sub>2</sub>SO<sub>4</sub> when sodium dichromate is obtained.

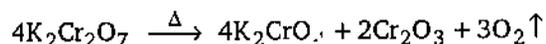


Now hot concentrated solution of sodium dichromate is treated with calculated quantity of potassium chloride when potassium dichromate is obtained.

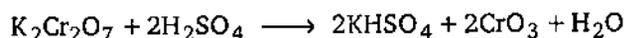


**Properties (i)** : K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is an orange red crystalline solid, melting point 398°C. It is less soluble in cold water but is more soluble in hot water.

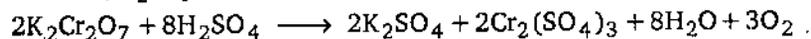
(ii) **Action of heat** : On heating at high temperature, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is decomposed to give chromate, chromic oxide and oxygen.



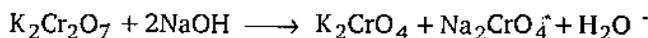
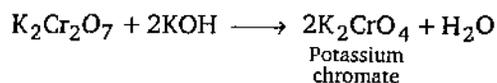
(iii) **Action of conc. H<sub>2</sub>SO<sub>4</sub>** : With cold acid, red crystals of chromic anhydride are obtained.



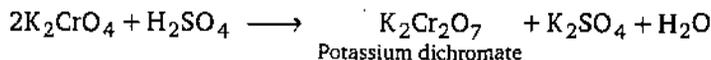
On heating the mixture, O<sub>2</sub> is produced.



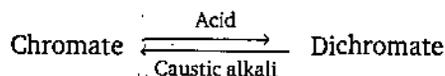
(iv) **Action of caustic alkalis** : Chromates are formed.



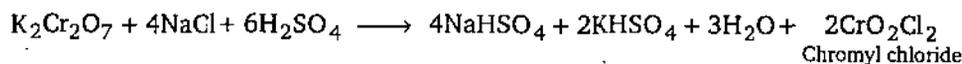
The yellow solution of chromate when acidified gives orange red solution of dichromate.



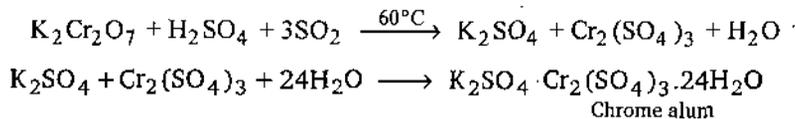
Thus, chromates and dichromates are interconvertible.



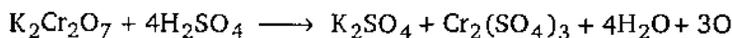
(v) **Formation of chromyl chloride** : Potassium dichromate when heated with a soluble chloride salt and conc.  $\text{H}_2\text{SO}_4$ , gives orange red vapours of chromyl chloride.



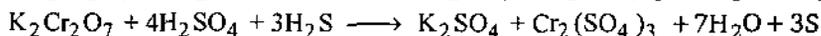
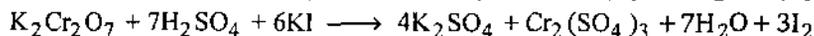
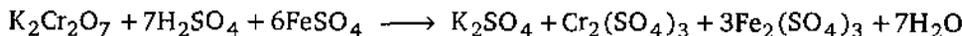
(vi) **Formation of chrome alum** : Chrome alum is formed when  $\text{SO}_2$  gas is passed through acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution at about  $60^\circ\text{C}$ .



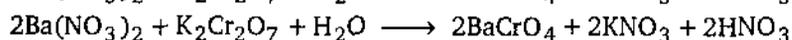
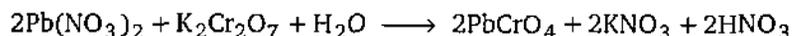
(vii) **Oxidizing properties** :  $\text{K}_2\text{Cr}_2\text{O}_7$  acts as an oxidizing agent in the acidic medium according to the equation :



Thus,  $\text{K}_2\text{Cr}_2\text{O}_7$  oxidizes ferrous sulphate to ferric sulphate, KI to  $\text{I}_2$ ,  $\text{H}_2\text{S}$  to S, HCl to  $\text{Cl}_2$  and ethyl alcohol to acetaldehyde.



(viii) **Action with lead and barium salt solutions** : Yellow precipitates of lead and barium chromates are obtained.



**Uses** :  $\text{K}_2\text{Cr}_2\text{O}_7$  is used :

(i) In inorganic analysis for the test of  $\text{Cl}^-$  and  $\text{SO}_3^{2-}$  radicals.

(ii) In oxidation-reduction titrations.

(iii) As oxidizing agent in inorganic chemistry.

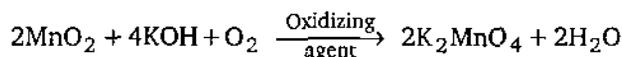
(iv) In dyeing and calico printing.

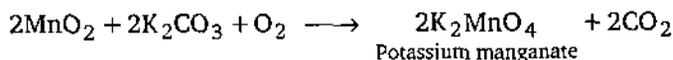
## • 10.5. POTASSIUM PERMANGANATE, $\text{KMnO}_4$

**Preparation** :

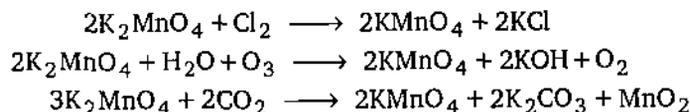
**From pyrolusite** : Pyrolusite is impure  $\text{MnO}_2$ . From this, the preparation of  $\text{KMnO}_4$  involves the following two steps :

(a) **Conversion of pyrolusite into potassium manganate** : The concentrated pyrolusite is fused with potassium hydroxide or potassium carbonate in the presence of air or an oxidizing agent like  $\text{KNO}_3$ ,  $\text{KClO}_3$  when green mass of potassium manganate is obtained.

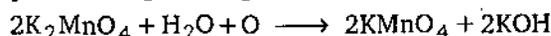




**(b) Conversion of potassium manganate into potassium permanganate :**  
Potassium manganate is extracted with water and then treated with  $\text{Cl}_2$ ,  $\text{O}_3$  or  $\text{CO}_2$  when  $\text{KMnO}_4$  is obtained.



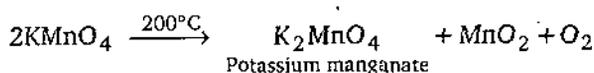
Now a days, the oxidation of potassium manganate into potassium permanganate is done electrolytically. The solution of potassium manganate is electrolysed in a cell between iron electrodes. The oxygen liberated at the anode converts potassium manganate into potassium permanganate.



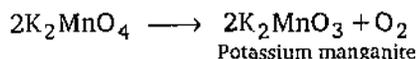
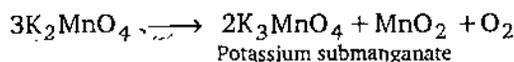
The violet solution of  $\text{KMnO}_4$  is carefully concentrated and crystallized.

**Properties :** (i)  $\text{KMnO}_4$  is a dark violet crystalline solid which is isomorphous with  $\text{KClO}_4$ . It dissolves in water giving violet solution.

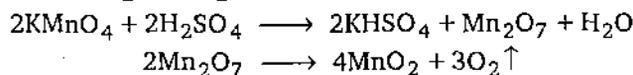
(ii) **Action of heat :** On heating at  $200^\circ\text{C}$ ,  $\text{KMnO}_4$  is decomposed to give  $\text{O}_2$ .



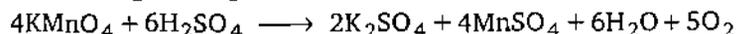
On further heating at  $500\text{--}700^\circ\text{C}$ , it decomposes according to the equation :



(iii) **Action of conc.  $\text{H}_2\text{SO}_4$  :** With cold acid, manganese heptoxide is formed which is decomposed to give  $\text{MnO}_2$  and  $\text{O}_2$ .

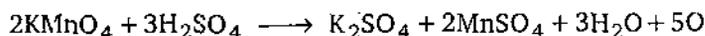


On heating with conc.  $\text{H}_2\text{SO}_4$ ,  $\text{O}_2$  is evolved.

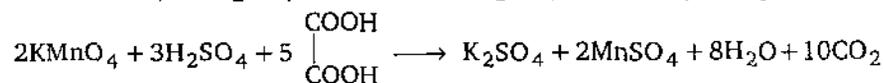
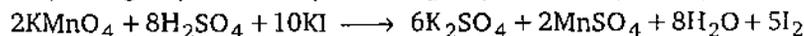
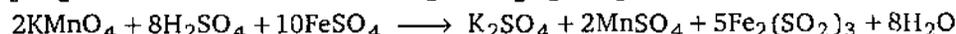


(iv) **Oxidizing properties :**  $\text{KMnO}_4$  is a strong oxidizing agent and acts as an oxidizing agent in acidic, alkaline and neutral mediums.

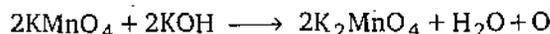
(a) **In the acidic medium :** In the acidic medium,  $\text{KMnO}_4$  behaves as :



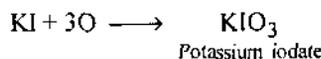
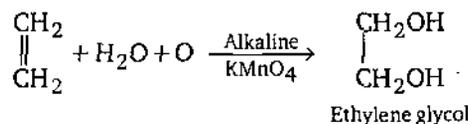
Thus,  $\text{KMnO}_4$  oxidizes ferrous sulphate to ferric sulphate, potassium iodide to  $\text{I}_2$  oxalic acid to  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  to S, nitrite to nitrate,  $\text{HCl}$  to  $\text{Cl}_2$  and  $\text{H}_2\text{O}_2$  to  $\text{O}_2$ .



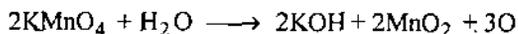
(b) **In the alkaline medium :** In this medium,  $\text{KMnO}_4$  behaves as :



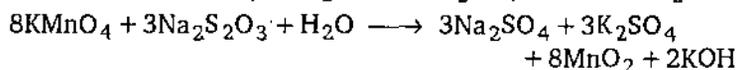
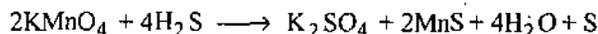
Thus,  $\text{KMnO}_4$  oxidizes ethylene to ethylene glycol and  $\text{KI}$  to  $\text{KIO}_3$ .



(c) **In the neutral medium** : In this medium,  $\text{KMnO}_4$  behaves as :



Thus,  $\text{KMnO}_4$  oxidizes  $\text{H}_2\text{S}$  to  $\text{S}$  and sodium thiosulphate to sodium sulphate.



**Uses** :  $\text{KMnO}_4$  is used :

(i) In the oxidation-reduction titrations for the estimation of ferrous salts, iodide salts, oxalic acid and  $\text{H}_2\text{O}_2$ .

(ii) As disinfectant, germicide and for purifying the water of stinking wells.

(iii) In the qualitative analysis for the test of  $\text{C}_2\text{O}_4^{2-}$  radical.

(iv) Alkaline  $\text{KMnO}_4$  is used as Bayer's reagent in organic chemistry.

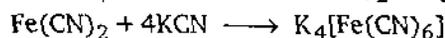
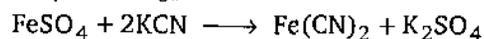
(v) In the preparation of  $\text{Cl}_2$  in the laboratory.

## • 10.6. POTASSIUM FERROCYANIDE, $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$

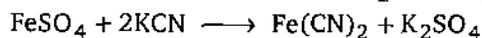
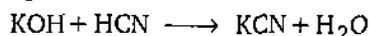
**(Potassium hexacyanoferrate (II) trihydrate)**

**Preparation** :

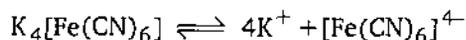
(i) By adding an excess of  $\text{KCN}$  to  $\text{FeSO}_4$  solution when a brown precipitate of ferrous cyanide first formed dissolves to form  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .



(ii) Commercially,  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is prepared by passing coal gas, which contains 0.2–0.3%  $\text{HCN}$ , through a solution of  $\text{FeSO}_4$  and  $\text{KOH}$ .  $\text{KOH}$  absorbs  $\text{HCN}$  to form  $\text{KCN}$  which then reacts with  $\text{FeSO}_4$  to form  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .

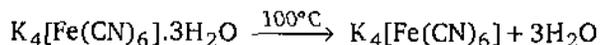


**Properties** : (i)  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is a lemon yellow crystalline solid, readily soluble in water. In the solution it ionizes as :

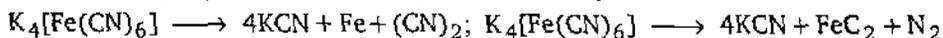


The complex ion is very stable and, therefore, it does not give the usual tests of  $\text{Fe}^{2+}$  ions.

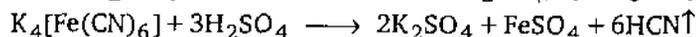
(ii) **Action of heat** : The hydrated salt,  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  becomes anhydrous and colourless on gentle heating at  $100^\circ\text{C}$ .



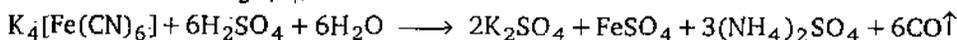
On strong heating  $\text{K}_4[\text{Fe}(\text{CN})_6]$  decomposes according to the equations :



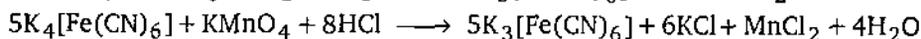
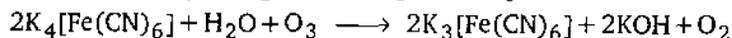
(iii) **Action of  $\text{H}_2\text{SO}_4$**  : When boiled with dil.  $\text{H}_2\text{SO}_4$ , hydrogen cyanide is evolved.



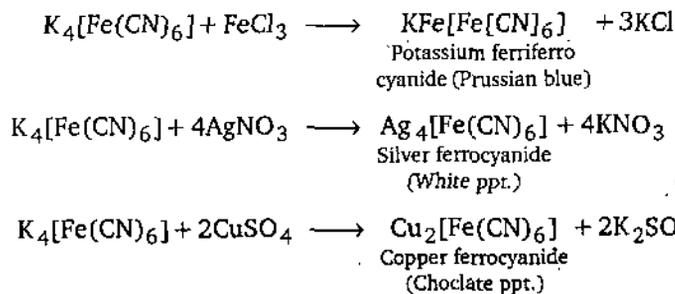
But with hot conc.  $\text{H}_2\text{SO}_4$ ,  $\text{CO}$  is evolved.



(iv) **Reducing properties** :  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is a reducing agent and is oxidized to potassium ferricyanide by oxidizing agents such as  $\text{Cl}_2$ ,  $\text{O}_3$ , acidified  $\text{KMnO}_4$ , acidified  $\text{H}_2\text{O}_2$  etc.



(v) **Formation of other ferrocyanides** :  $\text{K}_4[\text{Fe}(\text{CN})_6]$  reacts with  $\text{FeCl}_3$ ,  $\text{AgNO}_3$ ,  $\text{CuSO}_4$ ,  $\text{ZnCl}_2$  to form complex salts.



**Uses :**  $K_4[Fe(CN)_6]$  is used :

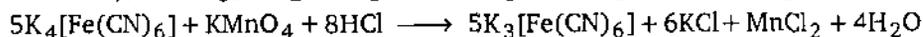
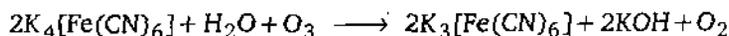
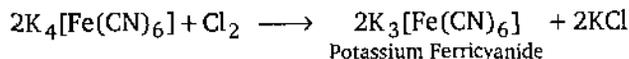
- (i) As a laboratory reagent for the test of  $Cu^{2+}$  and  $Fe^{3+}$  ions.
- (ii) In the preparation of carbon monoxide.
- (iii) In the preparation of potassium ferricyanide and prussian blue. Prussian blue is a useful pigment for laundry purposes.

### • 10.7. POTASSIUM FERRICYANIDE, $K_3[Fe(CN)_6]$

#### [Potassium hexacyanoferrate (III)]

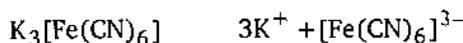
**Preparation :**

$K_3Fe(CN)_6$  is prepared by the oxidation of potassium ferrocyanide solution by  $Cl_2$ ,  $O_3$ , acidified  $KMnO_4$  or acidified  $H_2O_2$  solution.



The solution on concentration and cooling deposits the red crystals of potassium ferricyanide.

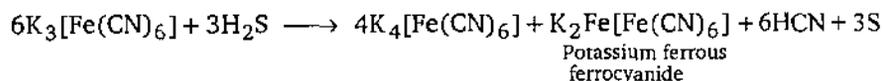
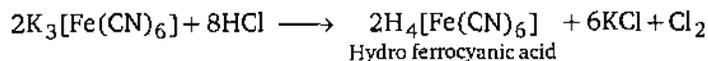
**Properties :** (i)  $K_3Fe(CN)_6$  is a dark red crystalline solid. It is readily soluble in water and gives a yellow solution. In solution it ionizes as :



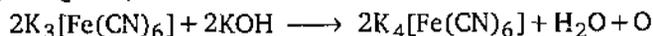
The complex ion is very stable and, therefore, it does not give the usual tests of  $Fe^{+3}$  ions.

(ii) **Oxidizing properties :** It is reduced to potassium ferrocyanide, and, therefore, it acts as an oxidizing agent.

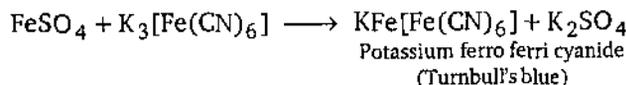
(a) In an acidic medium,  $K_3Fe(CN)_6$  oxidizes  $HCl$  to  $Cl_2$  and  $H_2S$  to  $S$ .



(b) In an alkaline medium,  $K_3Fe(CN)_6$  oxidizes  $H_2S$  to  $S$ ,  $H_2O_2$  to  $O_2$ ,  $SO_2$  to  $H_2SO_4$ ,  $PbO$  to  $PbO_2$  and  $Cr_2O_3$  to  $K_2CrO_4$ .



(iii) **Action with ferrous salts :**  $K_3Fe(CN)_6$  gives a deep blue precipitate of Turnbull's blue with ferrous salt solution.



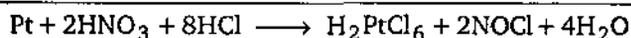
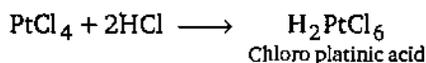
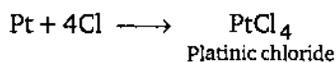
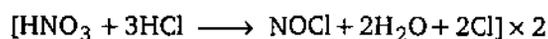
**Uses :**  $K_3Fe(CN)_6$  is used :

- (i) As a laboratory reagent.
- (ii) As an external indicator in the titration of  $Fe^{2+}$  ions against  $Cr_2O_7^{2-}$  ions.

## • 10.8. CHLORO PLATINIC ACID, $H_2PtCl_6 \cdot 6H_2O$

### Preparation :

Platinum is dissolved in aqua regia. The solution so obtained is boiled with conc. HCl to remove excess of  $HNO_3$ . The resulting solution is concentrated and cooled when crystals of chloroplatinic acid are obtained.



**Properties :** (i) Chloroplatinic acid is a reddish brown crystalline solid. It is soluble in water and gives bright yellow solution.

(ii) **Acidic nature :** Chloroplatinic acid is a strong dibasic acid and ionizes according to the equation :

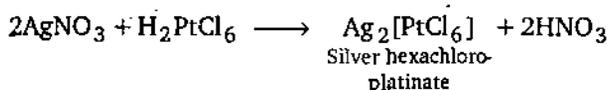
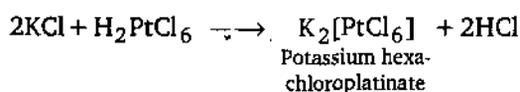
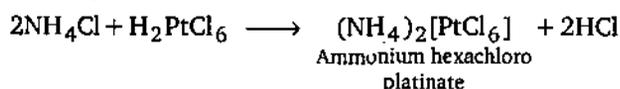


It gives hexachloro platinate salts.

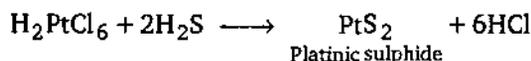
(iii) **Effect of heat :** On heating in the presence of  $Cl_2$ ,  $H_2PtCl_6$  gives  $PtCl_4$  at  $370^\circ C$  and  $PtCl_2$  at  $580^\circ C$ .



(iv) **Formation of chloroplatinate salts :**  $H_2PtCl_6$  forms hexachloroplatinate salts with ammonium, potassium and silver salt solutions.



(v) **Action with  $H_2S$  :** A black precipitate of platinic sulphide is obtained.

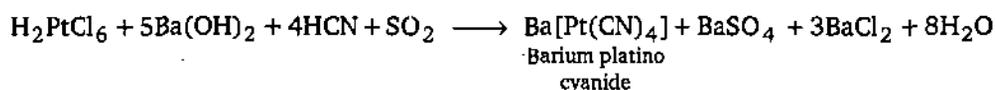


(vi) **Action with organic bases :**  $H_2PtCl_6$  reacts with organic bases to form stable crystalline compounds.



This crystalline compound on heating gives platinum. The process can be used for determining equivalent weight of organic bases.

(vii) **Formation of barium platino cyanide :** When the solution of chloro platinic acid is boiled with  $Ba(OH)_2$  and HCN and then  $SO_2$  gas is passed, barium platino cyanide is formed.



**Uses :**  $H_2PtCl_6$  is used :

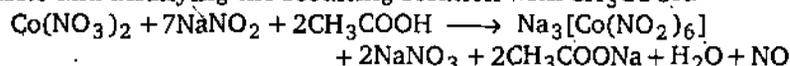
- (i) In determining equivalent weight of organic bases.
- (ii) In the qualitative and quantitative analysis of ammonium and potassium.
- (iii) In photography and in the preparation of other platinum compounds.

### • 10.9. SODIUM COBALTINITRITE, $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$

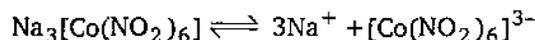
#### [(Sodium hexanitritocobaltate (III))]

##### Preparation :

Sodium cobaltinitrite is obtained by mixing well cooled solutions of cobalt nitrate and sodium nitrite and acidifying the resulting solution with  $\text{CH}_3\text{COOH}$ .

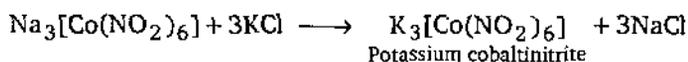
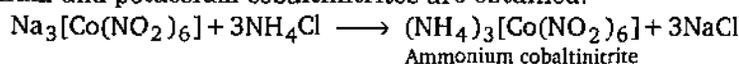


**Properties :** (i)  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$  is a yellow crystalline solid, soluble in water. In solution, it ionizes as :



The complex ion is very stable and, therefore, it does not give the usual tests of  $\text{Co}^{3+}$  ions.

(ii) **Action with ammonium and potassium salts :** Yellow precipitates of ammonium and potassium cobaltinitrites are obtained.



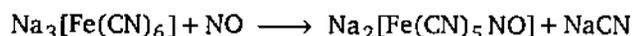
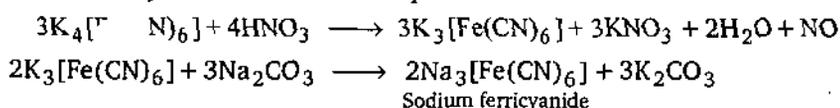
**Uses :** Sodium cobaltinitrite is used as a reagent for the detection and estimation of ammonium and potassium salts.

### • 10.10. SODIUM NITRO PRUSSIDE, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$

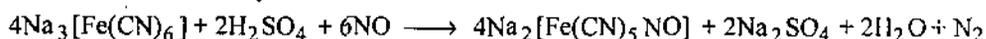
#### [(Sodium pentacyanonitrosylferrate (III) dihydrate)]

##### Preparation :

(i) Sodium nitroprusside is prepared by heating potassium ferrocyanide with 50%  $\text{HNO}_3$  when ferrocyanide is oxidized to ferricyanide and a brown solution is obtained. The resulting solution is cooled when  $\text{KNO}_3$  crystallizes out and is removed. The remaining solution is neutralized with  $\text{Na}_2\text{CO}_3$ , concentrated and then cooled when ruby red rhombic crystals of sodium nitroprusside are obtained.

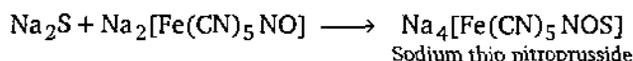


(ii) Sodium nitroprusside may also be obtained by passing  $\text{NO}$  through the acidified solution of sodium ferricyanide.

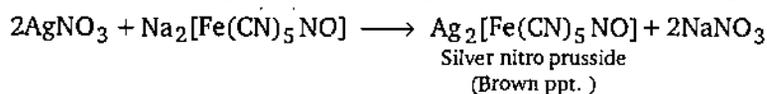


**Properties :** (i) Sodium nitroprusside is a ruby red crystalline solid, readily soluble in water. Its solution decomposes on standing, hence it is freshly prepared when required.

(ii) **Action with sulphides :** The freshly prepared solution of the compound gives purple colouration with alkali metal sulphides.



(iii) **Action with  $\text{AgNO}_3$  :** A brown precipitate of silver nitroprusside is obtained.



(iv) **Action with ketones :** Methyl ketones give deep red colour with sodium nitroprusside in the presence of alkali.

**Uses :** Sodium nitroprusside is used as a reagent in the qualitative analysis for the test of sulphide radical and is also used for the test of methyl ketones.



### • TEST YOURSELF

- Describe the preparation, important properties and uses of the following compounds :
  - Titanium dioxide
  - Titanium tetrachloride
  - Chromyl chloride
  - Potassium dichromate
  - Potassium permanganate
  - Potassium ferrocyanide
  - Potassium ferricyanide
  - Chloroplatinic acid
  - Sodium cobaltinitrite
  - Sodium nitroprusside
- What happens when (give equations also) ?
  - Titanium dioxide is heated with carbon and chlorine.
  - Titanium tetrachloride is hydrolysed.
  - Potassium dichromate is heated with sodium chloride and conc.  $\text{H}_2\text{SO}_4$ .
  - Potassium dichromate is treated with ferrous sulphate in presence of an acid.
  - Potassium permanganate is heated.
  - Potassium permanganate is treated with ferrous sulphate in an acidic medium.
  - Oxalic acid is treated with potassium permanganate in presence of  $\text{H}_2\text{SO}_4$ .
  - Potassium permanganate is treated with sodium thiosulphate solution.
  - Potassium ferrocyanide is treated with ozone.
  - Potassium ferrocyanide is reacted with ferric chloride solution.
  - Potassium ferrocyanide is treated with  $\text{H}_2\text{O}_2$  in an acidified solution.
  - Chloroplatinic acid is heated.
  - Chloroplatinic acid is treated with silver nitrate solution.
- What is Etard's reaction ?
- In the acidic medium  $\text{KMnO}_4$  is reduced to :
  - $\text{Mn}^{2+}$
  - $\text{Mn}^{4+}$
  - $\text{Mn}^{6+}$
  - None of the above
- Potassium ferrocyanide on heating with conc.  $\text{H}_2\text{SO}_4$  forms :
  - $\text{HCN}$
  - $\text{CO}$
  - $\text{SO}_2$
  - $\text{SO}_3$
- On heating a mixture of  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{NaCl}$  with conc.  $\text{H}_2\text{SO}_4$ , orange red vapours are evolved. These are of :
  - $\text{CrOCl}_2$
  - $\text{CrO}_2\text{Cl}$
  - $\text{CrO}_2\text{Cl}_2$
  - $\text{Cr}_2\text{OCl}_2$
- On passing  $\text{SO}_2$  in an acidified solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ , it turns green due to the formation of :
  - Potassium chromate
  - Chromium sulphite
  - Chromic sulphate
  - Chromous sulphate
- When pyrolusite is fused with  $\text{KOH}$  in the presence of air, it gives :
  - $\text{KMnO}_4$
  - $\text{K}_2\text{MnO}_4$
  - $\text{Mn}(\text{OH})_2$
  - $\text{Mn}_3\text{O}_4$
- Fill in the blanks :
  - In acidic medium, the equivalent weight of  $\text{KMnO}_4$  (Mol. wt. =  $M$ ) is .....
  - The external indicator used in the titration of  $\text{Fe}^{2+}$  ions against  $\text{Cr}_2\text{O}_7^{2-}$  ions is .....
  - When ..... is heated spongy platinum is obtained.
  - When ..... is treated with  $\text{HCl}$ , chlorine is formed.
  - On heating potassium permanganate at  $200^\circ\text{C}$ , ..... is formed.

### ANSWERS

4. (a) 5. (b) 6. (c) 7. (c) 8. (b)  
 9. (i)  $M/5$ ; (ii) potassium ferricyanide (iii)  $(\text{NH}_4)_2[\text{PtCl}_6]$  (iv)  $\text{KMnO}_4$   
 (v) potassium manganate.